10

Illustrated World of Science Encyclopedia

Chemistry I:
THE ELEMENTS

THE WORLD OF SCIENCE

VOLUME
10
CHEMISTRY I
The Elements

with

The Illustrated Science Dictionary

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CHICAGO

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VOLUME 10

CHEMISTRY I

The Elements

THE ORDER OF ATOMS | periodic classification of the elements

PERIODIC TABLE OF THE ELEMENTS

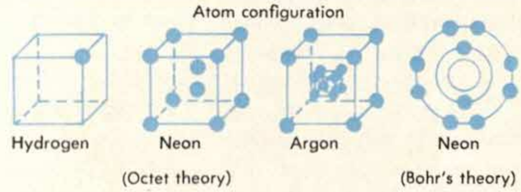
Groups	O	I	II	III	IV	V	V
Period I	Atomic number Symbol Element Atomic weight	1 **H** hydrogen 1.008 −252.8 −259.14					
Period II	2 **He** helium 4.003 −268.9 −272.2	3 **Li** lithium 6.940 1330 186	4 **Be** beryllium 9.013 2970 1278	5 **B** boron 10.82 2550 2300	6 **C** carbon 12.011 4200 3550	7 **N** nitrogen 14.008 −195.8 −209.86	183 −218.4
Period III	10 **Ne** neon 20.183 −245.9 −248.67	11 **Na** sodium 22.9910 880 97.5	12 **Mg** magnesium 24.32 1107 651	13 **Al** aluminum 26.98 2057 659.7	14 **Si** silicon 28.09 2355 1420	15 **P** phosphorus 30.975 280 44.1	4.60 .25
Period IV	18 **Ar** argon 39.944 −185.7 −189.2	19 **K** potassium 39.1 760 62.3 29 **Cu** copper 63.54 2336 1083	20 **Ca** calcium 40.08 1240 842 30 **Zn** zinc 65.38 907 419.47	21 **Sc** scandium 44.96 2750 1850 31 **Ga** gallium 69.72 1983 29.78	22 **Ti** titanium 47.90 3000 1800 32 **Ge** germanium 72.60 2700 958.5	23 **V** vanadium 50.95 3000 1710 33 **As** arsenic 74.91 615 subl	24 **Cr** chromium 52.01 688 220
Period V	36 **Kr** krypton 83.80 −152.9 −156.6	37 **Rb** rubidium 85.48 700 38.5 47 **Ag** silver 107.873 1950 960.8	38 **Sr** strontium 87.63 1150 774 48 **Cd** cadmium 112.41 767 320.9	39 **Y** yttrium 88.92 3300 1820 49 **In** indium 114.82 2000 156.4	40 **Zr** zirconium 91.22 2900 1857 50 **Sn** tin 118.70 2270 231.9	41 **Nb** niobium 92.91 3700 2500 51 **Sb** antimony 121.76 1380 630.5	42 **Mo** molybde 95.95 1390 452
Period VI	54 **Xe** xenon 131.30 −107.1 −112.9	55 **Cs** cesium 132.91 670 28.5 79 **Au** gold 197.0 2600 1063	56 **Ba** barium 137.36 1140 725 80 **Hg** mercury 200.61 356.58 −38.87	57 **La** lanthanum 138.92 4500 1193 81 **Tl** thallium 204.39 1457 302	72 **Hf** hafnium 178.50 3200 1700 82 **Pb** lead 207.21 1620 327.43	73 **Ta** tantalum 180.95 4100 2996 83 **Bi** bismuth 209.00 1560 271.3	74 **W** tungsten 183.86 600
Period VII	86 **Rn** radon (222) 61.8 −71	87 **Fr** francium (223)	88 **Ra** radium (226) 1140 700	89 **Ac** actinium (227) 1050			

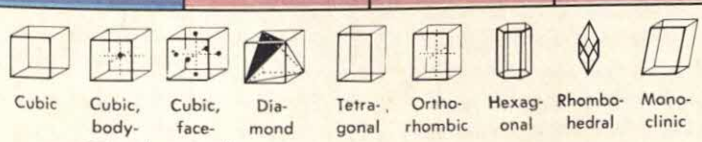
Conventional representation of crystal structures

boiling point

melting point

	VII	VIII		
		Atom configuration		
8 O oxygen 16.000	9 F fluorine 19.00			
16 S sulfur 32.066	17 Cl chlorine 35.457			
...um 2480 1890	manganese 1900 1260	26 Fe iron 55.85 3000 1535	27 Co cobalt 58.94 2900 1455	28 Ni nickel 58.71 2900 1455
34 Se selenium 78.96	35 Br bromine 79.916			
...enum 4800 2620	43 Tc technetium (99)	44 Ru ruthenium 101.1 2700+ 2450	45 Rh rhodium 102.91 2500+ 1966	46 Pd palladium 106.4 2200 1549.4
52 Te tellurium 127.61	53 I iodine 126.91 184.35 113.7			
...n 5900 3370	75 Re rhenium 186.22 — 1367	76 Os osmium 190.2 5300 2700	77 Ir iridium 192.2 4800 2454	78 Pt platinum 195.09 4300 1773.5
84 Po polonium (210)	85 At astatine (210)			





LANTHANIDE SERIES	ACTINIDE SERIES
58 cerium Ce 140.13 3200 1077	90 thorium Th 232.05 4500 1845
59 praseodymium Pr 140.92 3290 1208	91 protactinium Pa (231) 1873
60 neodymium Nd 144.27 3450 1297	92 uranium U 238.07 3818 1132
61 promethium Pm (145) 3000 1570	93 neptunium Np (237) 640
62 samarium Sm 150.35 1900 1325	94 plutonium Pu (244) 3235 639.5
63 europium Eu 152.0 1700 1150	95 americium Am (243) 2607 850
64 gadolinium Gd 157.26 3000 1520	96 curium Cm (248)
65 terbium Tb 158.93 2800 1638	97 berkelium Bk (257)
66 dysprosium Dy 162.51 2600 1670	98 californium Cf (251)
67 holmium Ho 164.94 2600 1770	99 einsteinium Es (254)
68 erbium Er 167.27 2990 1800	100 fermium FM (252)
69 thulium Tm 168.94 2400 1870	101 mendelevium Md (256)
70 ytterbium Yb 173.04 1800 1097	102 nobelium No (254)
71 lutetium Lu 174.99 2200 1970	103 lawrencium Lw (257)

Whether gas, liquid, or solid, every bit of matter in the universe is composed of atoms. When every atom in a bit of matter is identical in all respects, the matter is said to be an element. Thus, mercury in a frozen, solid state, or as the normally encountered silvery liquid, or as the gaseous vapor seen in street lights, is composed of identical atoms.

There are 92 natural elements scattered in varied amounts about the Earth, and a few more that have been created through applied nuclear physics. No matter what the source, each element has properties governed by a set of periodic laws—properties that distinguish it from all other elements.

One of the more important properties of an element is its ability to combine with other elements to form compounds. The tendency to combine is a chemical property, and is possessed to a greater or lesser degree by every element. Some elements, such as oxygen, show a vigorous combining power, while others show little or no ability to form compounds; the noble gases (helium, neon, argon, krypton, xenon, and radon) are examples of the latter.

While the noble gases are unique in their chemical inertness, the atoms of all other elements can be classified in groups according to the similarity of their chemical properties.

UNIFORMITY OF THE CHEMICAL CHARACTERISTICS OF ATOMS

In order to see the interrelationship of elemental groups, more is required than a simple listing of the elements by their chemical characteristics. For example, a characteristic shared by almost every element is the ability to combine with oxygen. A list prepared using this criterion would, for all practical purposes, contain all the elements except oxygen and the noble gases.

A more realistic approach is to assign each element an atomic number based on the extent of positive nuclear charge (also called proton charge). This method is chosen because the atoms of each element have a proton charge unique to that element. Thus, only hydrogen can have an atomic number of 1, helium an atomic number of 2, lithium an atomic number of 3, and so on through the natural and man-made elements.

Since the number of protons in an atom's nucleus determines its positive charge, it will also determine the extent of negative charge on the atom. This is true because a neutral atom contains as many negatively charged electrons as positively charged protons.

The electrons are arranged about the nucleus in a series of orbits extending outward from the nuclear mass. While the concept of orbital electrons is descriptive, it is not totally accurate because the positions of the electrons are not fixed. Rather, electrons can be found in a series of concentric shells that surround the nucleus. Each atom has from one to seven such shells, depending on the element. Furthermore, each shell may consist of an additional number of subshells, from one to four.

Only when the combined total of electrons in an atom's shells and subshells equals the positive nuclear charge is the atom neutral. However, in terms of chemical behavior it is only the outermost shell (the one farthest from the nucleus) and its electron complement that are of interest here.

Now, if all the elements are listed in ascending order of their atomic numbers, and the electron complement for each atom is added to the list, an interesting pattern emerges. First, with almost complete uniformity every eighth element appears to repeat the chemical or physical properties of the element that precedes it by eight places. Secondly, the outermost shell's electron configuration also tends to show repetition. These phenomena, called periodicity, form the basis of the periodic table of the elements.

THE PERIODIC TABLE OF THE ELEMENTS

In the development of the periodic table, the number eight is an important consideration. Generally, when the number of electrons in the atoms can be estimated by some multiple of eight, a new period of elements begins. Thus, the list of elements can be reworked into a series of horizontal lines (the periods) when any of the following conditions are met:

1. Whenever an element has eight electrons in its outermost shell;
2. Whenever there are less than eight outermost electrons, but when the next-to-outermost shell is complete;
3. Whenever the outermost shell contains zero or two electrons and the next-to-outermost shell contains 18 or 16 electrons, respectively.

Following these guidelines, the periodic table of the elements has been developed, as illustrated. Each element has been placed in its own square, and is shown in relation to all the other elements. Each position contains the name of the element and its chemical symbol (for example, H = hydrogen), the element's atomic number, and physical data such as atomic weight, melting and boiling points, and crystal structure.

The two columns on the right represent the so-called lanthanide series and the actinide series. Because they vary only slightly from their namesakes (lanthanum and actinium, respectively) they should be contained in the same squares.

Chemical properties repeat themselves in each column and vary consistently along each line.

GROUPS, PERIODS, AND VALENCE

Standing alone in Period 1, hydrogen is unique. It is the only element so situated. As can be seen, all other elements share a period. Element 2, helium, begins the second period. Like all the noble gases, helium has a complete outer shell. For this reason, the noble gases are really a group unto themselves, and could be represented separately on the periodic table. For the sake of uniformity, however, they are placed as the first elements in the periods.

The vertical columns represent groups whose members have similar chemical properties. Valence is the term used to describe the capacity of an element's atoms to combine with those of another element. The value of a given valence is determined by the number of electrons in the outermost shell in a neutral atom. It is important to note that some atoms in a chemical reaction lose their neutral status to become charged particles called ions. In so doing, the tendency is to gain or lose electrons to create a complete shell. Thus, if an atom loses electrons in a reaction, the net charge created is positive because the number of protons does not change. Conversely, a gain of electrons creates a negative charge.

The extent of an atom's, or ion's, valence is expressed by a figure equal to the number of hydrogen atoms with which the element can combine. Hydrogen's valence is a constant value of +1. Therefore, since two atoms of hydrogen combine with a single oxygen atom in the formation of water, oxygen has a valence of 2. Because in the process it is easier for oxygen to gain two electrons rather than release six (there are six electrons in oxygen's outermost shell), its valence is −2. On the other hand, when lithium combines with hydrogen, it readily gives up its single available electron, creating an extra positive charge of +1. Whether or not an element is reacting with hydrogen, the same rule applies.

Some elements have more than one valence, and all are dependent on the outer electron arrangement.

PLATINUM | a rare and useful metal

In 1735, while working with gold ores from Colombia, the Spanish scientist Antonio de Ulloa discovered a metal whose properties were similar to those of gold, but whose color was silver. Hence, the name platinum, from the Spanish *platina* for silver.

Though itself quite rare, platinum (Pt) is the most abundant of the so-called platinum group of metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum). These metals resemble one another closely in their chemical and physical properties, and are often found associated in deposits.

MAJOR PLATINUM DEPOSITS

In nature, platinum is found in the elemental state, either alone or mixed with other metals. As such, it occurs as grains or small nuggets. Because it has a very high specific gravity of 21.45 (meaning that its weight is 21.45 times that of water), it is easily separated from its crushed ores by sedimentation.

The major platinum deposits are in the form of alluvial clay, in which the metal appears as grains in the ratio of about 0.1 ounce per ton of clay. The richest deposits are in Canada and the Urals of the Soviet Union. Small quantities are also mined in the western United States where platinum occurs as a pure metal. Colombia, the source of its discovery, still contributes significantly to the world's platinum supply. In Canada, the metal is found combined with arsenic in the mineral sperrylite ($PtAs_2$), and is also associated with two other important metals: copper and nickel. Because of the economic importance of the latter elements, the commercial extraction of platinum is a routine matter. The relative scarcity of platinum is attested to by an annual world production on the order of 40 tons.

NATIVE PLATINUM—Elementary platinum is often found as grains, roundish masses, or nuggets.

EXTRACTION PROCESSES

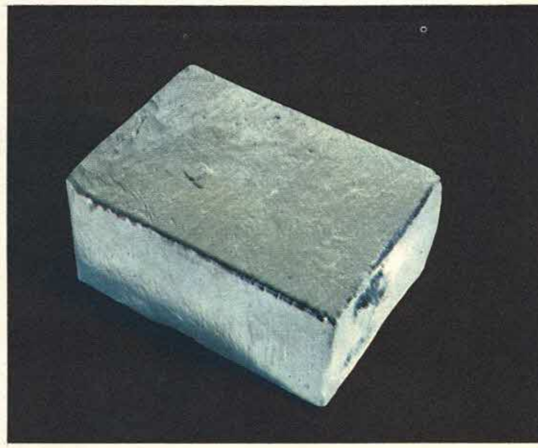
Where platinum has been deposited as a native element, mining is essentially a two-step operation. First, the metal is mined as the raw element along with rock or alluvial clay. Then, platinum is separated from any elements that are associated with it. The first part of this operation is mechanical, involving the breaking up of platinum-bearing rock and separation of the heavy metal with running water. The second operation, however, poses a more complex problem, since the metals associated with the platinum are close relatives. Thus, these metals have similar chemical properties, necessitating the use of special techniques for isolation of the platinum. These techniques subject the mixture of platinum and its associated metals to a series of chemical reactions that allow each to be separated.

A NOBLE METAL

Platinum, like gold and silver, is a so-called noble metal because it exhibits little tendency to change from the elemental metallic state to an ionic state. By contrast, sodium changes vigorously from its metallic form to an ionic state.

Platinum is totally unaffected by air or water at any temperature or by a majority of common oxidizing agents. This property explains why platinum oxide is not easily obtainable.

Platinum salts include the halides, a hydroxide, sulfate, and telluride among its more stable compounds. The chloride and iodide are important because of the complexes they form (for example, H_2PtCl_6). Such complexes are obtained by reacting platinum with an acid mixture, aqua regia, which consists of a mixture of concentrated nitric and hydrochloric acids—one of the few mixtures with which platinum forms compounds.



PLATINUM INGOT—Free of impurities, this ingot is ready for use in jewelry or analytical equipment.

Another important complex is barium platinocyanide, a fluorescent substance used in screens for radioscopic equipment. When struck by x-rays, this salt emits a greenish light due to excitation of its electrons.

Because of its almost total inertness, platinum is used to make specialized scientific equipment for use in chemical analysis. Some compounds, however, will attack the metal (in addition to aqua regia). Sodium and potassium hydroxides at temperatures above 400° C (752° F), cyanides, sulfides, and selenic acid all corrode platinum.

Lead, arsenic, antimony, and other metals can be dissolved in platinum, alloying with the metal well below its melting point: 1,773° C (about 3,223° F). The fusion of such metals in platinum containers thus means that the metal becomes contaminated and useless for further analytical purposes.

A SURPRISE PROPERTY

Metallic platinum is obtainable in a finely divided form called platinum black or

PLATINUM CRUCIBLES—Resistant to most types of corrosion, platinum crucibles such as these are used in chemical analysis.

platinum sponge. As such, it has the property of adsorbing large quantities of hydrogen, making it a valuable catalyst in hydrogenation reactions. In this form, the metal is used to obtain the most active molecular hydrogen/atomic hydrogen equilibrium ($H_2 \rightleftharpoons 2H$). Platinum catalysts can also be activated with oxygen.

Thus, platinum acts both as an oxidation catalyst and reduction catalyst. As such, it is used in the oxidation of ammonia (NH_3) to nitric oxide (NO), a reaction difficult to achieve with any other catalyst.

Since platinum is able to adsorb hydrogen, it also finds use in the purification of this gas. Here, a membrane of platinum acts as a one-way sieve, preventing passage of all but hydrogen molecules.

USES

Besides its chemical properties, platinum possesses extreme ductility and malleability. These physical characteristics are used in the making of extremely thin needles, wire, or plate—which may be as small as a few thousandths of a millimeter in cross section. One gram of the metal is sufficient to manufacture about 30 mi of wire having a diameter of 0.001 mm.

The coefficient of expansion of platinum is so slight that an object made of the pure metal will expand less than 0.000009 of its length per degree of temperature rise. This coefficient is identical to that of crown glass (used in optics), so the welding of the two poses no problems.

The electrical resistance and its temperature coefficient for platinum are relatively high for a metal, and the resistance of coils of pure platinum wire gives a precise measure of temperature. The international temperature scale from −190 to 660° C (−310 to 1,220° F) is defined

PLATINUM WIRE—The ductility of platinum allows it to be drawn into extremely fine wire.

in terms of such a platinum resistance thermometer. At higher temperatures, from 660 to 1,063° C (1,220 to 1,945° F)—the melting point of gold—the international temperature scale is defined by the electromotive force of a thermocouple with a wire of pure platinum against another of the alloy 90 percent platinum and 10 percent rhodium.

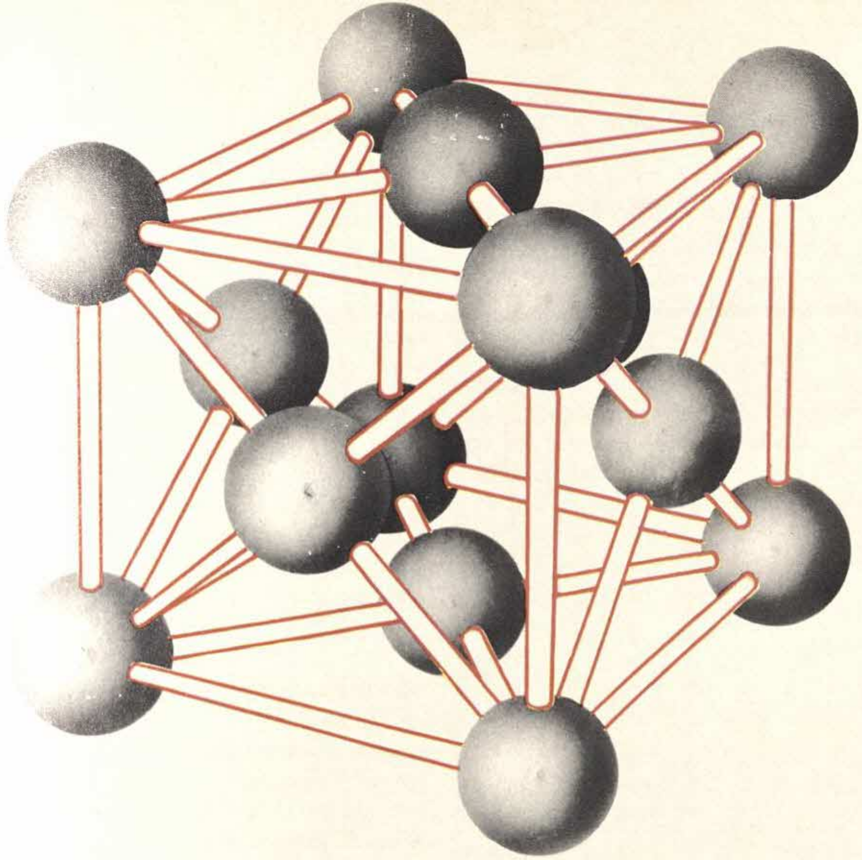
Platinum is used in preparing electrical contacts and sparking points because it resists the high temperature and chemical attack of electric arcs. The manufacture of dental alloys consumes large amounts

PLATINUM BLACK—Obtained by separating platinum from its salts, platinum black is used as a catalyst.

of the metal also. The prototype international standard meter of length and the standard kilogram of mass have been made from the alloy 90 percent platinum and 10 percent iridium. Platinum is used to electroplate fine laboratory weights and in the chemical industry for objects that must resist corrosion.

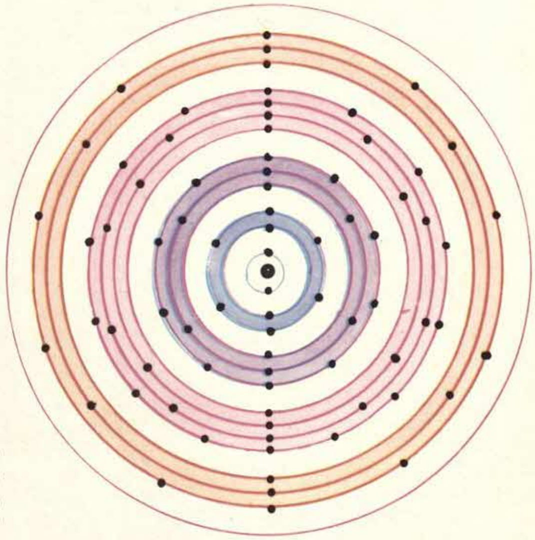
Similar in brilliance to silver, but lacking silver's tendency to tarnish, platinum finds extensive use in jewelry. Its malleability and ductility also make it very suitable for engraving—more so than white gold, a nickel-gold alloy used in place of platinum. However, platinum is costly, and used only in expensive settings.

Platinum black is obtained by the separation of the metal from solutions of its salts. Its black appearance is due to the microscopic size of platinum black, although the metal is as pure as its silvery counterpart. Microscopic platinum is important industrially as a catalyst, where many reactions can be accelerated. A kilogram of platinum black spread on woven asbestos is capable of combining thousands of cubic meters of nitrogen and hydrogen into ammonia every hour. Similarly, sulfur trioxide (used in making sulfuric acid) can be obtained from the combination of sulfur dioxide and oxygen.

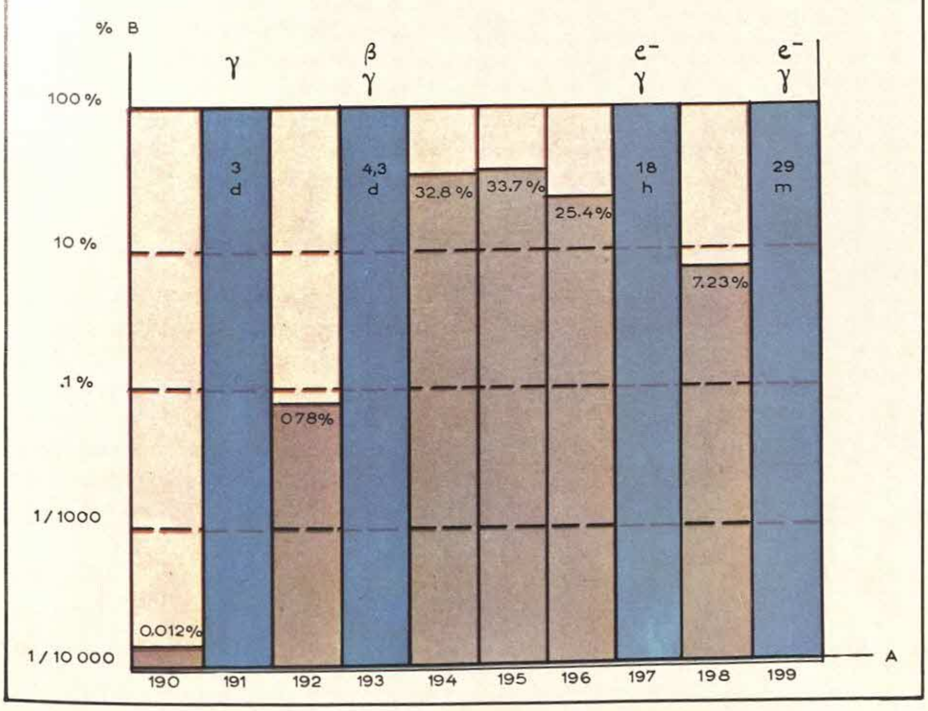


CRYSTALLINE STRUCTURE—Within metallic platinum, atoms are arranged in an orderly manner, one atom at each corner of a cube and one in the center of each face. A piece of platinum is made up of an enormous number of these cubes, each touching its neighbors in such a way that the cube faces are shared. The actual size of the cube in this illustration is such that a single face measures 3.9142 ten-millionths of a millimeter across.

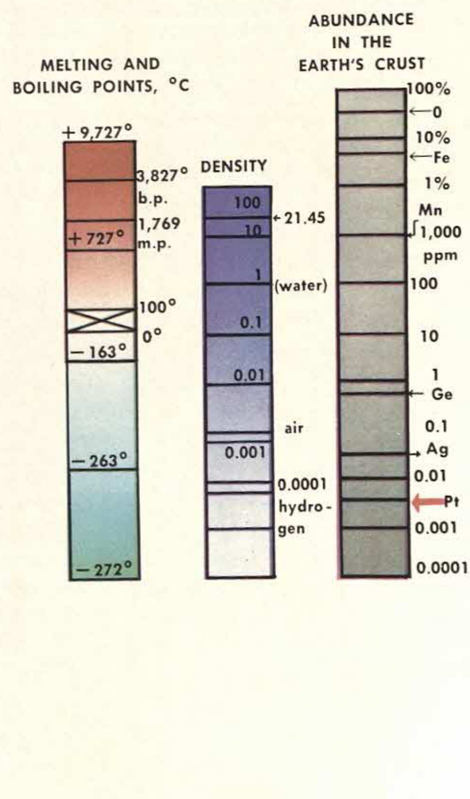
THE ELECTRON CONFIGURATION OF PLATINUM—The illustration represents the 78 electrons in position around a platinum nucleus. The electrons are arranged in orbits, or shells, at varying distances from the nucleus. In reality, the position of any electron at a given instant is not fixed, nor are the electrons in a two-dimensional plane.



PLATINUM ISOTOPES—With regard to electron arrangement, all platinum atoms are identical. However, not all nuclei are similar, and this accounts for an element's isotopes. In the illustration, the height of the gray column shows the relative abundance of the platinum isotopes. They differ from one another by virtue of their nuclear constitution; the nuclei always have the same number of positively charged protons (in a number equal to that of the electrons, in this case 78). However, the nuclei may contain differing numbers of neutrons—particles of zero charge that add only mass to the nucleus. Four combinations of protons and neutrons (those with mass numbers 191, 193, 197, and 199) do not form stable nuclei. Combinations of this type disintegrate spontaneously, producing radioactivity. Such nuclei are found in nature, but are produced artificially in atomic reactors.



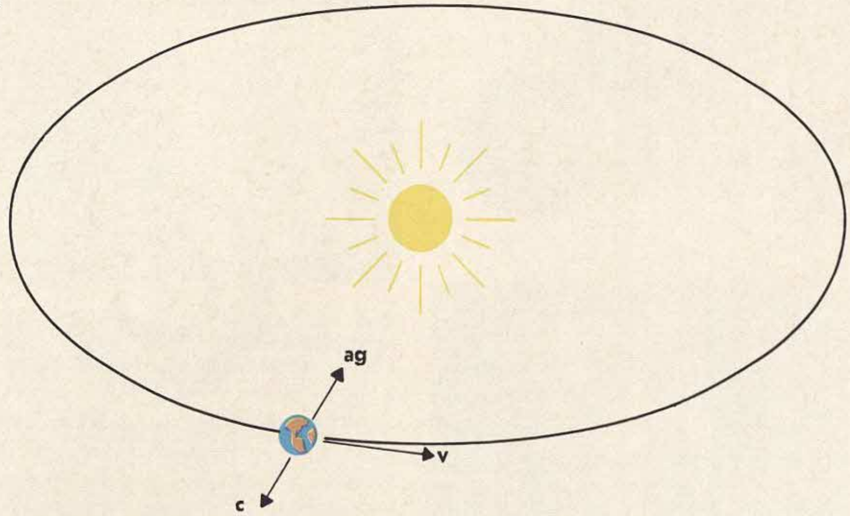
MELTING AND BOILING POINTS, DENSITY, AND ABUNDANCE IN THE EARTH'S CRUST—In this illustration, the density of platinum is compared to that of water, air, and hydrogen, while its natural occurrence is contrasted to that of iron, manganese, germanium, and silver.



HYDROGEN | the smallest atom

As early as the beginning of the present century, scientists had reached the conclusion that matter consisted of the union of atoms. It was also believed that these atoms were of different kinds, although their number was fairly limited when compared with the huge number of compounds found in nature. By 1900, many of the elements had been identified. The mystery at that time was how the single particles (the atoms—those indivisible units identical in each element but different in different elements) were constructed and the nature of more elementary particles (if any) making up the atoms.

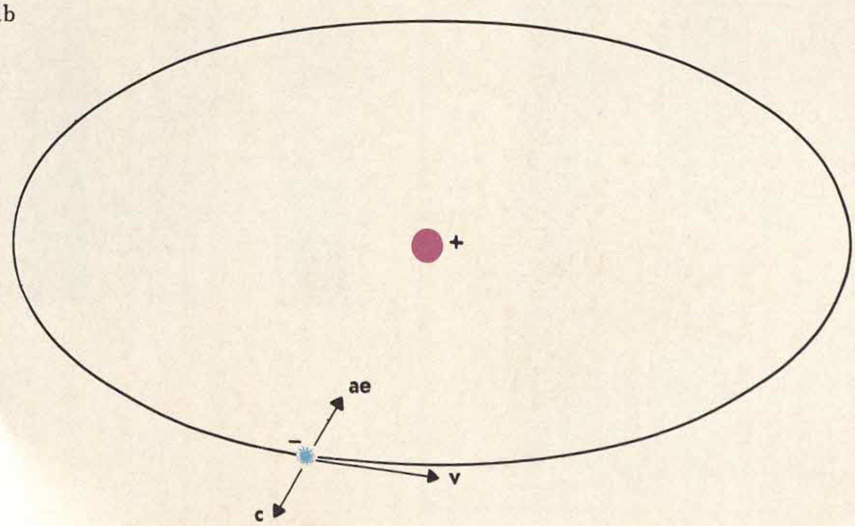
1a



A PLANET REVOLVING AROUND THE SUN— Suppose from a point in space one could observe the sun and the Earth for a year. During this time, the Earth would carry out one revolution around the sun, moving in a somewhat circular orbit, as shown in Illustration 1a. At the moment in which the observation was begun, the Earth was traveling in the direction indicated by arrow **v.** If there were no sun, the Earth would continue to travel in a straight line in space in the direction of this arrow. However, it actually moves in a circle, which means that its direction is continually changing. As it is obliged to move in a circle, the Earth is subjected to a centrifugal force **c,** which continuously tends to push it out of its orbit. This force is the reaction to the force of gravity **ag** attracting the Earth toward the sun. The sun has a huge mass and its force of gravitational attraction **ag** is enough to prevent the Earth from moving away from it.

AN ELECTRON REVOLVING AROUND A PROTON—If an electron could be seen revolving around a proton, the same activity as was shown in the preceding illustration might be observed: one sphere revolving around another sphere in a circular orbit. As shown in Illustration 1b, **c** is the centrifugal force acting on the electron, **ae** is the force attracting it toward the nucleus, and **v** is the velocity and the direction in which it is traveling. As in the previous illustration, the force attracting the electron toward the center of its orbit (toward the proton) is equal to the centrifugal force. The difference lies in the nature of the force binding the electron to the proton; in this case it is an electrical force. The proton is positively charged and the electron is negatively charged. These two equal and opposite charges attract each other and the closer they are together, the greater the attraction. The attractive force is equal to the centrifugal force. The two forces are in equilibrium and the electron revolves around the proton in a circular orbit.

1b



The first scientist to shed light on this problem was the English physicist Ernest Rutherford. In 1912, he conducted his now famous experiment on the diffusion of alpha particles through metal foils. This was the first of a long series of similar experiments, resulting in the initial concepts of the structure of matter.

The atom consists essentially of a part in which the mass is concentrated and which is positively charged (the nucleus) and of another part that has almost no mass and is negatively charged (the electrons). The electrons neutralize the positive charge of the nucleus and are distributed around it, occupying a large volume.

The German physicist Hans Wilhelm Geiger repeated Rutherford's experiment on different metal foils (copper, silver, and platinum) and with very accurate measurements was able to calculate the nuclear charge of the metals themselves. When the charge of the nucleus for each of the known elements had been determined, it was found that the elements could be ordered by charge into a "periodic system." It was found that this arrangement by charge coincided almost exactly with that table of elements drawn up by the Russian chemist Dmitri Mendeleev in 1869, in which he used atomic weight as the criterion for arrangement. It was, therefore, logical to choose the simplest element—hydrogen (H)—as a starting point for research into the internal structure of atoms.

A TINY SOLAR SYSTEM

The Danish physicist Niels Bohr first arrived at the conclusion that the negative particle—which has only a tiny mass (electron) and must lie on the outside of the nucleus (a single proton)—rotates around the nucleus in a well-defined orbit. Bohr imagined the hydrogen atom as resembling a tiny solar system in which

the nucleus (proton) is the sun and the electron is its tiny planet rotating around it (Illustration 1). Bohr limited his analogy with the planetary system to this single aspect. It was later postulated that the electron orbit could not be of any particular size whatever, as in the case of the planets, but that its radius must have certain values. Only in these values is the condition fulfilled whereby the electron dissipates no energy in traveling around its orbit.

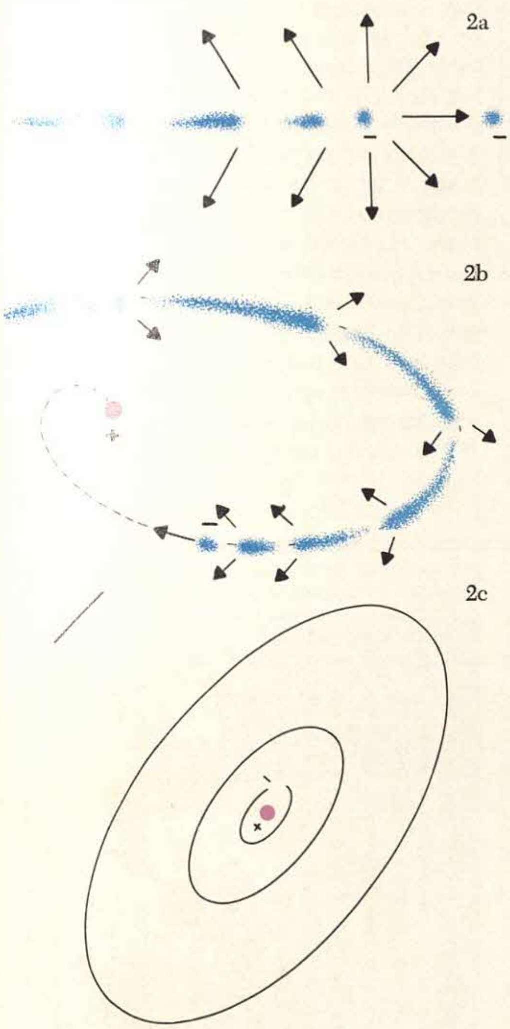
Electron orbits are said to be quantized, in that they behave as predicted by the quantum theory. This theory interprets the tiny world of the atom as a system in which the electrons can occupy only orbits having certain values if the electrons are not to lose energy. This is in contrast with the classical Maxwell-Lorentz theory (developed by the Scottish physicist James Maxwell and the Dutch physicist Hendrik Lorentz), which states that an electric charge in uniform motion, in a line that is not straight, must give off electromagnetic energy (Illustration 2).

In the hydrogen atom, the electron is normally in a circular orbit having a radius of 0.53 Å (Ångstroms). It is then said to be in the fundamental or ground state. The other possible orbits are larger and the electron can enter them only if it has a certain energy value that is greater than its energy in the fundamental state. This additional energy is received from the outside, in the form of thermal or other excitation.

The same quantity of energy will be emitted in the form of light when the electron returns from an outer orbit to an inner one having less energy. It follows, then, that the various jumps the electron makes in returning to inner orbits should correspond to the emission of a well-defined quantity of energy. In terms of light energy, these jumps should correspond to certain wavelengths, and thus to certain colors, of the light emitted.

The study of the emission spectrum of hydrogen and the lines appearing in it—light having certain wavelengths—has provided much evidence in support of Bohr's theory. This is an excellent example of an a posteriori confirmation of a bold, new theory.

The spectral lines mentioned above are grouped into various series: the Lyman series, which lies in the ultraviolet region; the Balmer series, consisting of visible radiation; and the Paschen and the Brackett series, which lie in the infrared region. The lines correspond to elec-



ELECTRONS RADIATING ENERGY—Suppose an electron is shot against another similarly charged particle (another electron) so that it comes to a stop. The kinetic energy of the electron due to its motion is transformed into electromagnetic energy. The electromagnetic radiation given off takes the form of a radio wave, visible light, ultraviolet radiation, or x-rays, depending on the amount of energy to be dissipated. X-rays have the highest energy and are only obtained by slowing down very fast particles; the other radiations have progressively less energy and come from slower particles (Illustration 2a).

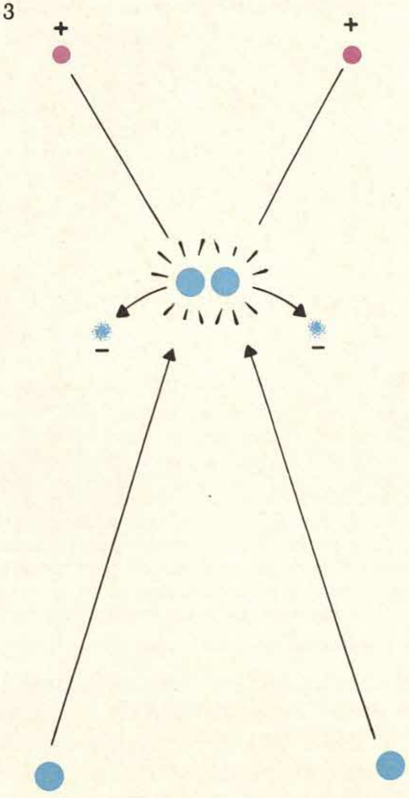
If a charged particle (for example, an electron) is made to pass near another oppositely charged particle (for example, a proton), the electron deviates from its path and in doing so gives off energy in the form of electromagnetic radiation, as shown in Illustration 2a. In Illustration 2b the electron is slowed down and instead of traveling in an orbit of the kind shown in Illustration 1b, it falls into the nucleus after following a spiral trajectory.

When accelerated, slowed down, or deviated, an electric charge gives off the energy it possessed in the form of radiation. Why does this not happen in the hydrogen atom?

The electron of the hydrogen atom can only stay in certain orbits. The electron revolving around the proton in a hydrogen atom does not radiate its energy if it is contained in certain orbits. It is usually to be found in the first orbit, which has a diameter of less than 1 Å (one hundred-millionth of a centimeter, which is the diameter of the hydrogen atom under normal conditions). On the other hand, if the hydrogen atom is involved in a collision, the electron may be bounced into an orbit having a larger diameter than that mentioned above (Illustration 2c). However, the electron does not stay in this orbit; it returns as soon as possible to the one having a diameter of less than 1 Å. This is why all hydrogen atoms are identical.

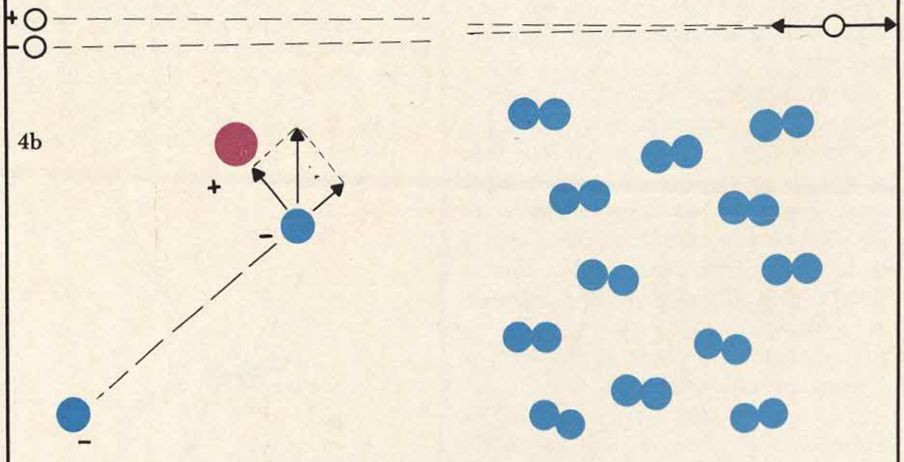
THE COLLISION OF HYDROGEN ATOMS—If two hydrogen atoms smash into each other violently enough, the electrons can be separated from the nuclei. However, if these separate particles approach each other closely enough, they join up to form new hydrogen atoms.

3



4a

4b



ATTRACTION AND DISTANCE — An electron placed at a great distance from a hydrogen atom is not appreciably affected electrically. It is repelled by one charge as much as it is attracted by the other. In effect, the two forces balance each other out (Illustration 4a). At a very short distance from the two particles making up a hydrogen atom, a third particle is attracted strongly by one particle and repelled weakly by the other (Illustration 4b).

If two hydrogen atoms are separated by a distance approximately equal to the diameter of the sphere of the atom, a strong enough attraction exists to bind them together. These atoms then form molecules (Illustration 4c). The origin of this force of attraction has not been examined in depth here. It is sufficient to know that it exists—that the atoms are linked in pairs when hydrogen gas is held at an ordinary temperature—and that it is produced by the electrical charges of the individual particles forming the atoms.

tron jumps from the outermost orbits to the first (fundamental state), second, third, and fourth orbits, respectively. All the series are present in an ordinary hydrogen emission spectrum because (statistically speaking) all possible energy transitions are taking place in any given group of hydrogen atoms.

Emission spectroscopy has always been a guide to the electron state of all atoms. Their orbits, even after Bohr's theory was superseded, have always been indicated with the letters s, p, d, and f, which stand for sharp, principal, diffuse, and faint and which are used to classify the intensity of the light radiation corresponding to the electron jumps generating the radiation. Each element or atom has as many characteristic spectra as it has electrons. Line spectra are characteristic of atoms or ions, while band spectra originate in molecules.

SOMEWHAT DIFFERENT HYDROGEN ATOMS

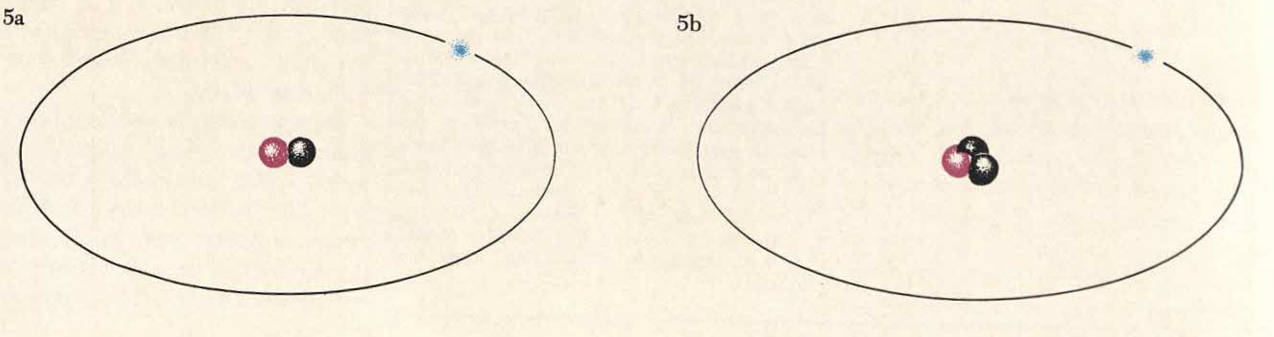
The hydrogen proton (also called th nucleus, because it lies at the center c the atom), is 1,836 times heavier than th electron revolving about it; both particl carry an electrical charge. If the hydr gen nucleus were heavier and its char remained unchanged, the resulting ato would have the same chemical properti as normal hydrogen, because the electr and its bonding (electrostatic attractio to the nucleus determine the chemic properties.

If a neutron is bonded to a proton, particle is obtained whose mass is near twice that of the proton, but who charge is no different from that of t proton alone; this particle is the deuter (see Illustration 5). If two neutrons a bonded to a proton, the mass will b three times that of the proton alone an the charge will remain unchanged; suc a particle is the triton (Illustration 5 A single electron revolving around a de teron or triton results in an atom who properties are the same as those of a atom of hydrogen. These atoms a named deuterium and tritium, respe tively, and are called isotopes of hydr gen. The tritium isotope is unstable an therefore radioactive. It emits negati beta particles of 19,000 electron vol energy and has a half-life of 12.5 year Both deuterium and tritium are useful isotopic tracers in the investigation chemical and biochemical reactions.

ISOTOPES OF HYDROGEN: DEUTERIUM AND TRITIUM—An atom composed of a deuteron (a particle formed by combining a neutron and a proton) and an electron is known as heavy hydrogen or deuterium (Illustration 5a). One hydrogen atom in 6,000 is a deuterium atom. An atom having as its nucleus a particle composed of a proton and two neutrons and surrounded by a single electron is known as tritium (Illustration 5b). A few tritium atoms are produced on the Earth as a result of bombardment by cosmic rays. These tritium atoms are short-lived, however, as their nuclei disintegrate easily (one neutron remains closely bound to a proton, but not two).

5a

5b



CADMIUM | from pigments to alloys to nuclear reactors

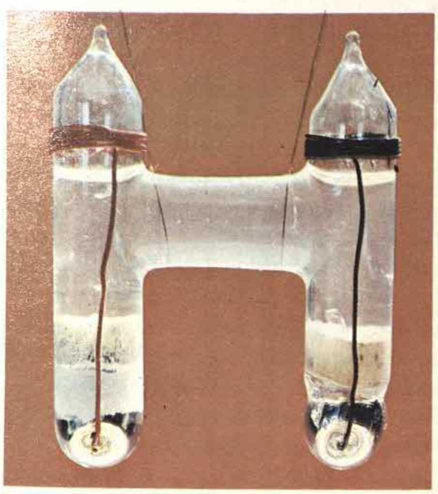
Cadmium (Cd) is a relatively rare metal in the Earth's crust, and is found almost exclusively in association with the ores of other elements. It has been estimated that if cadmium were evenly distributed in the lithosphere, it would account for about 0.1 gram per ton.

Most often, cadmium occurs in small quantities associated with copper, lead, and zinc ores, and is obtained as a by-product of the treatment of these minerals. The only cadmium mineral of any commercial importance is the sulfide, greenockite (CdS).

The history of cadmium is most closely linked with that of zinc, which the ancients used to form alloys with copper. However, the zinc was never separated from its ores before use, so that all the impurities, including cadmium, went into the finished product. It was this quirk of history that kept the chemistry of cadmium hidden for thousands of years. When research into zinc included unwittingly observation of all the impurities included in its ores.

In 1817, the German chemist-mineralogist Friedrich Strohmeyer made some observations of zinc carbonate. In a chemical reaction typical of iron, the carbonate produced a yellow substance. However, investigation showed that iron was not the cause, nor was zinc. In fact, Strohmeyer had found a new element whose reactions parallel in some respects those of iron. Since his discovery was a result of the work with zinc carbonate, he named it cadmium, from the ancient Greek word *kadmeia* for calamine (zinc carbonate).

WESTON CELL—This cell, as described in the text, provides a constant electromotive force of 1.0183 volts at 18° C (64.4° F).



EXTRACTION OF CADMIUM

Metallic cadmium is obtained primarily as a by-product of the smelting of zinc, copper, and lead ores, and on occasion by treating the cadmium sulfide mineral greenockite. In the processing of zinc ores, for example, cadmium occurs as a dark brown oxide. This compound is isolated and heated with carbon to reduce it to the raw metal. The metal is further purified by electrolysis.

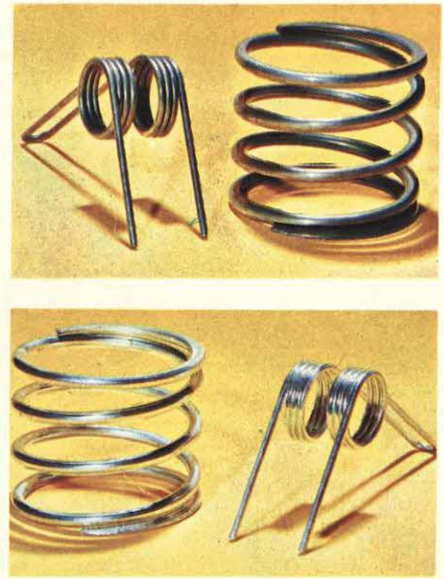
Cadmium is a soft, bluish-white metal similar in many ways to zinc. Exposed to the atmosphere, its shiny luster becomes dull, due to oxidation.

Caution should be used when working with cadmium and its soluble compounds. The fumes from the heated metal or the compounds are toxic, and the present maximum allowable concentration in air has been established as 0.1 milligram per liter.

CHEMICAL CHARACTERISTICS AND COMMON COMPOUNDS

Chemically, cadmium behaves much like zinc. Both, for example, exhibit a bivalence. Some cadmium compounds also react in a manner similar to iron, which can mask the presence of cadmium.

Cadmium sulfide is a brightly colored compound that, among others, forms the basis for the orange-yellow pigment called cadmium yellow. Heated at standard atmospheric pressure, the salt will decompose. However, if heated to 1,700° C (3,092° F) at a pressure of 100 atmospheres, the sulfide melts without decomposition. Careful cooling of the molten material allows the formation of large crystals having an index of refraction higher than that of diamond, although their clarity is impaired when thicknesses are excessive.



CADMIUM PLATING—To protect these springs from corrosion, the raw metal in the top illustration is electroplated with cadmium.

Cadmium sulfide crystals are semiconductors, and are able to rectify electric current—properties similar to those of germanium and selenium. These properties are exploited by the electronics industry.

Cadmium sulfate, $CdSO_4$, is another important compound, finding use in ophthalmology as a treatment for certain eye diseases. In electronics, this compound is used to make Weston cells, which are used as a standard of electromotive force. Such a cell can be represented in the following way:

$$\underset{\text{amalgam}}{Cd(Hg)} \mid \underset{\text{saturated solution}}{CdSO_4 \cdot \tfrac{8}{3} H_2O}, \underset{\text{saturated solution}}{Hg_2SO_4} \mid Hg.$$

The cell is able to supply a constant, standard voltage that does not vary from an electromotive force of 1.0183 volts at 18° C (64.4° F). Such cells are not used primarily as a power source, but to test the accuracy of other equipment in the laboratory, or where precise electronic measurements are paramount, as in physics.

When compounded with selenium, cadmium forms the intense red pigment cadmium selenide. This, mixed with cad-

mium sulfide, produces a broad range of color, from vibrant yellow through orange to a deep red.

A combination of cadmium and nickel is used to produce a type of dry battery having two distinct advantages over the common lead type. First, such batteries require no solution for operation, and second, they need not be disconnected when they run down. (Lead batteries must be disconnected to prevent damage to themselves and to the equipment they power.) One drawback to more widespread use of nickel-cadmium batteries is their cost. This factor usually restricts their use to expensive equipment, as in sophisticated photographic and scientific apparatus.

Although metallic cadmium, either alloyed or in the pure form, is used in a number of ways, the metal's greatest use is in plating. Iron is protected from corrosion by the electrolytic deposition of a thin layer of cadmium on its surface. Essential to the process is a rigorous degreasing and cleaning of the base metal (iron). If this is omitted or poorly done, parts of the iron will not accept the cadmium and will remain exposed to corrosion. The layer of cadmium need be no thicker than a fraction of a millimeter to afford protection. With time, the cadminum itself becomes covered with a brown oxide, but this in no way affects its protective qualities.

For economic reasons, only delicate parts made of iron are cadmium-plated. Similar protection is afforded by galvanizing, or zinc plating, of noncritical parts at considerably less cost.

Low melting and antifriction alloys contain a large quantity of cadmium. Two such alloys with very low melting points are Lipowitz's metal and Wood's metal, both of which have a melting point of 70° C (158° F). Their compositions are:

	cadmium	bismuth	lead	tin
Lipowitz's metal	10.0%	50.0%	26.7%	13.3%
Wood's metal	12.5%	50.0%	25.0%	12.5%

Because they melt at such a low temperature, these alloys can be used for soldering delicate instrument parts. It is interesting to note that the melting points of such alloys are considerably lower than those of the constituent metals.

The so-called antifriction alloys that cadmium forms with other materials are used to make bearings whose coefficient of friction is quite low. One common application for such materials is in the automobile engine. Antifriction bearings provide the surface on which the shaft rotates. Should normal lubrication become insufficient, these bearings can prevent damage to the shaft from abrasion.

Because these alloys are soft (in comparison to steel), they can be subjected to relatively dirty conditions while continuing to function. Within an automotive engine, for example, any impurities resulting from combustion that find their way from the cylinders to the drive shaft can be absorbed by the bearings. If such impurities were not absorbed, scoring of the shaft would result in considerable damage to the engine.

CADMIUM AND NUCLEAR TECHNOLOGY— The rectangular bars are made of cadmium plate encased in a strong aluminum jacket. They can be positioned so that the technicians are able to control the neutron flow within the reactor. Because cadmium can absorb great quantities of neutrons, the reaction can be kept going at a constant rate, or stopped completely.

CADMIUM AND NUCLEAR REACTORS

One of the principles on which a nuclear reactor is based is the unimpeded diffusion of neutrons within the reactor. In order to maintain a nuclear reaction, these neutrons are absorbed by the nuclear fuel (uranium or plutonium, for example). Certain materials, however, will absorb neutrons without maintaining the reaction, and one of cadmium's isotopes is such a material. The proper balance of neutrons, nuclear fuel, and neutron dampers is, therefore, necessary to prevent a controlled nuclear reaction from becoming an uncontrolled nuclear reaction—an atomic bomb.

Cadmium-113, the isotope used as a damper, can absorb tremendous quantities of slow neutrons at a very rapid rate. Although other elements have similar neutron-absorbing capabilities, cadmium remains the preferred choice, with an absorbing power ten thousand times more efficient than aluminum. Cadmium was first used in nuclear technology by the Italian-American physicist Enrico Fermi, who constructed the first nuclear reactor at the University of Chicago in 1943.

IRON | one of the Earth's most useful metals

A silvery-white metal in its pure state, iron (Fe) is the second most abundant of the Earth's metals and the fourth most abundant element. The core of the Earth is composed largely of metallic iron. In the crust of the Earth, however, iron has reacted with other substances, and is seldom found in its pure state except in meteorites or as minute specula in basaltic rocks.

All plants, animals, and human beings require iron to live. In human beings the largest percentage of iron is in the red blood cells, where it forms an essential part of hemoglobin. Small quantities are also found in the muscles and the tissues.

The chemical symbol for iron, *Fe*, is derived from the Latin *ferrum*, meaning "iron." Iron has an atomic number of 26 and an atomic weight of 55.85. It has a specific gravity of 7.86.

Iron is the basic material for thousands of manufactured goods, from small pins to mammoth buildings. It combines readily with nonmetals such as sulfur and oxygen. Enormous quantities—far more than any other metal—are used in alloys. Steel—one of the most useful and cheapest metals—is produced by adding a small amount of carbon to iron.

Several precious stones, including topaz, turquoise, and spinel, contain iron.

IRON ORES

Iron is smelted from several oxidized minerals found in large quantities in the crust of the Earth; these minerals include hematite, magnetite, limonite, and the carbonate siderite.

Hematite (Fe_2O_3) is an ore consisting of 70 percent iron and 30 percent oxygen. Its name derives from its blood-like color and the Greek word for blood. Sometimes hematite occurs in the rhombohedral form (Illustration 2a), sometimes in the form of thin sheets resembling the petals of a rose (Illustration 2b) and sometimes in a powder called red ocher, which is used as a pigment (Illustration 2c).

Magnetite (Fe_3O_4) which derived its name from its magnetic properties, consists of about 72 percent iron, making it the richest iron ore. It crystallizes in rhombohedral and octahedral shapes (Illustration 3). Magnetite can also be formed by alteration of rocks such as olivine and biotite, which have been chemically corroded by water and gases in solution.

Limonite ore accounts for a considerable percentage of the world production of iron. A sample is shown in Illustration 4. Its chemical formula, $Fe_2O_3 \cdot nH_2O$, indicates that it contains variable quantities of water crystallized into its mass. The percentage of iron in each sample of limonite depends on the number of molecules of water it contains. Formed by the alteration of other iron ores—chiefly siderites and pyrites—limonite often originates from deposits of solutions of ferruginous water (water containing dissolved iron minerals). The action of microorganisms known as iron bacteria has also resulted in deposits of huge quantities of limonite. The deposits in Alsace-Lorraine—the largest in Europe—are of this type.

Siderite is a ferrous carbonate with the formula $FeCO_3$. It consists of 43 percent iron. Its crystals are rhombohedral (Illustration 5). When unaltered, siderite is white, but it turns yellowish or brown when oxidized. Siderite is formed by chemical alteration of rock or in conjunction with various types of sedimentary rock.

Goethite, an iron hydroxide with the formula $FeO(OH)$, is associated with limonite. It is found in needle-shaped crystals or in layers.

Large quantities of iron are also extracted from pyrite (iron disulfide, FeS_2), shown in Illustration 6. Pyrite is burned with an excess of air—a process called roasting—to make sulfur dioxide, which is then used to produce sulfuric acid and iron oxides suitable for iron extraction.

1

GABBRO—This type of rock often contains iron or iron compounds.

IRON DEPOSITS

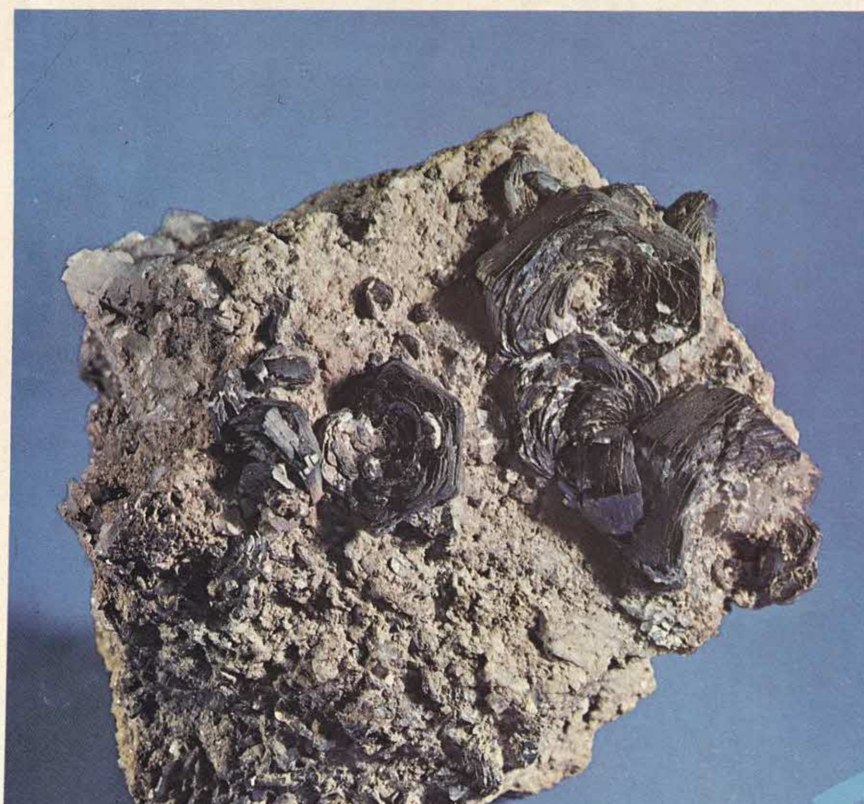
Location of the chief iron deposits in the world is shown on the map in Illustration 7. The United States is the largest producer of iron. While iron is found in every state, the most important deposits are the hematite ores in Michigan, Minnesota, and Wisconsin—particularly around Lake Superior. The largest man-made hole in the world, located near Hibbing, Minnesota, is the result of an iron mine.

Many European countries, including the Soviet Union, are also big producers of iron. Large deposits of limonite in Lorraine provide France with a rich and economical source of iron. The chief Russian deposits are at Perm in the Urals, and at Krivoi Rog in the Ukraine. In Britain, iron ore deposits are found among the coalfields of the Midlands and northern England. Sweden has extensive deposits, as do Germany, Spain, Luxembourg, Canada, and India. In recent years immense deposits have also been discovered in Africa, particularly in Liberia, Morocco, and western Algeria.

The history of many iron ore deposits is one of rise and fall, with many falling into disuse after centuries of exploitation and others coming into their own after cen-

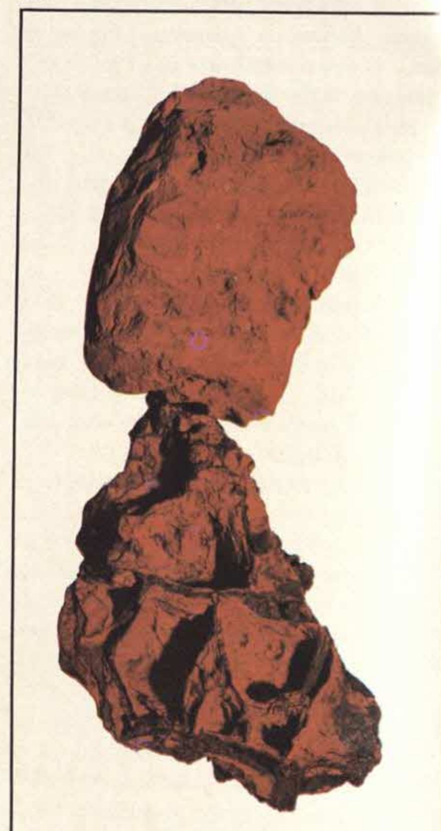
2a

2b



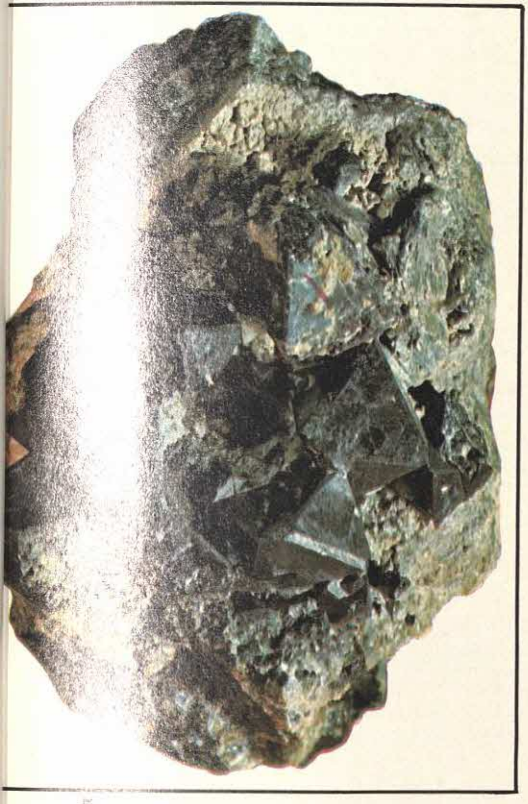
IRON ORES—The most important of the ores of iron, hematite (Illustration 2a) reduces very readily to metallic iron. Hematite is found in brown rhombohedral crystals. In Illustration 2b, hematite is shown in thin lustrous sheets arranged like fossilized rose petals. A common form of ferric oxide, Fe_2O_3, red ocher (shown in Illustration 2c) is earthy and powdery, and contains a high percentage of iron.

2c



MAGNETITE—A saline magnetic ferrosoferric oxide, this ore is a natural magnet.

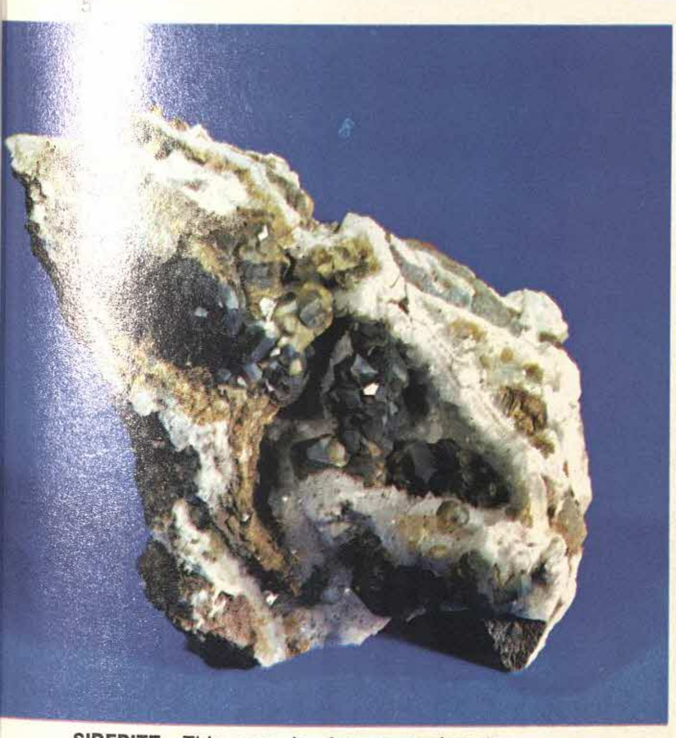
3



LIMONITE—The chemical formula for limonite is $Fe_2O_3 \cdot nH_2O$. It contains variable quantities of crystallized water.

4

5

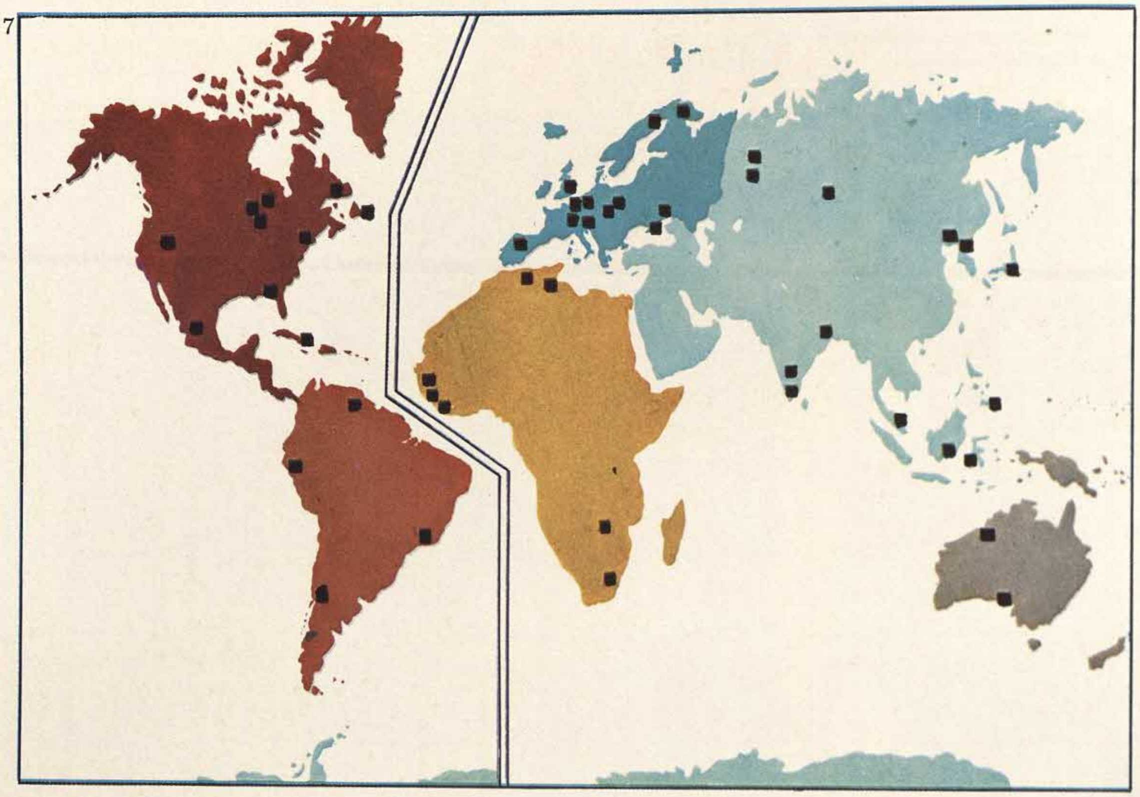


SIDERITE—This ore is ferrous carbonate, $FeCO_3$. Its white rhombohedral crystals may turn yellowish or brown due to alteration.

6

PYRITE—The formula for pyrite (iron disulfide) is FeS_2. Its crystals are golden yellow and are often cubic in shape.

7



ABUNDANCE OF IRON IN THE WORLD — In Europe, Lorraine is very rich in minette, a form of limonite. The Ruhr, Upper Silesia, northern Spain, the Soviet Union, Sweden, and Britain all have important iron deposits, and large deposits have recently been discovered in Africa. The United States produces the most iron.

turies of neglect. In the past, extraction techniques were such that only very pure ores yielded good quality metal. Thus, small deposits such as those in the foothills of the Alps in Lombardy were mined heavily since Roman times because of the purity of their ores. Today, these small deposits are almost totally ignored. On the other hand, despite the great size of the deposits in Lorraine, the phosphorus content of the ores made it impossible to mine any but the worst metal until the last century, when new refining techniques permitted extraction of the metal in blast furnaces.

Today, because of progress in metal-finishing techniques, a deposit, in order to be profitable, must be large and lend itself to open-cut mining—that is, mining on the surface rather than underground.

IRON COMPOUNDS

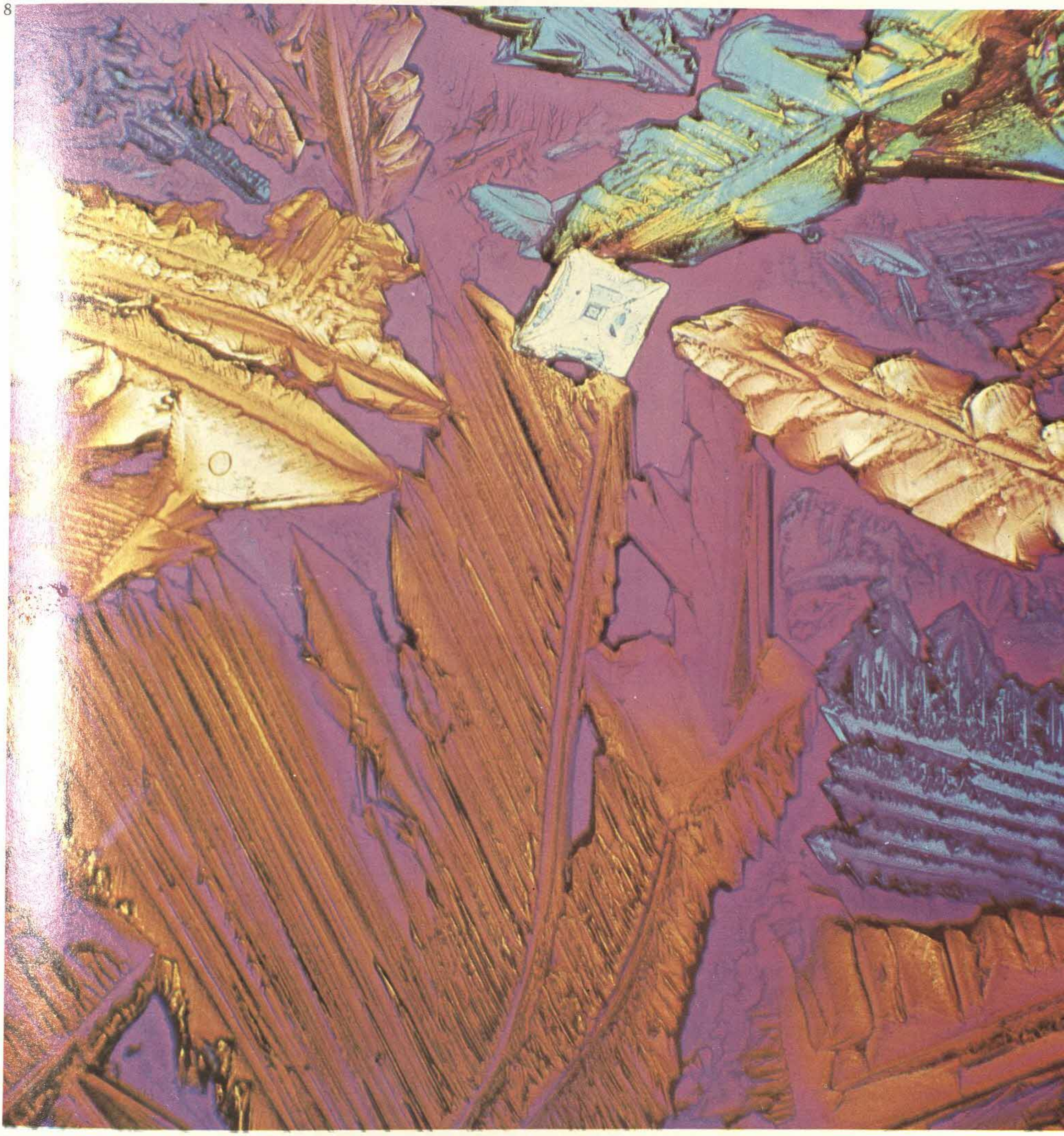
Iron has oxidation numbers of +2 and +3 in its chief compounds. It reacts with oxygen in the air to produce ferrous oxide—FeO—also called iron(II) oxide, which is somewhat unstable and tends to turn into ferric oxide—Fe_2O_3—called iron (III) oxide. Ferric oxide can be produced by burning iron in an excess of air. Sulfides of iron include ferrous sulfide, FeS, produced through the interaction of hydrogen sulfide—H_2S—and salts of iron in the presence of ammonia.

Dissolving iron in sulfuric acid produces the pale green ferrous sulfate $FeSO_4$, which on contact with air rapidly turns into the brown-colored ferric sulfate $Fe_2(SO_4)_3$. When combined with hydrochloric acid—HCl—iron produces ferrous chloride $FeCl_2$, which is white in the anhydrous (waterless) state and green in the tetrahydrated state. Iron combined with chlorine produces ferric chloride—$FeCl_3$—a blackish-red compound with green tints. When this compound reacts with water, it turns a golden yellow and becomes $FeCl_3 \cdot nH_2O$.

THERAPEUTIC USE

In the treatment of hypochromic anemias, iron has its most important therapeutic use. The iron deficiency condition impairs the formation of hemoglobin and may impair other functions of the red blood cells. Any of a large number of iron compounds may be used in therapy, and inorganic salts are equally effective for the purpose.

8



FERROUS SULFATE—Broken spears? A colorful example of modern art? Precious stones? This piece of ferrous sulfate, crystallized from a water solution, is shown as it appears in polarized light. (25 X)

COBALT AND NICKEL | vital elements of importance for the aircraft industry

As mentioned in the articles on transition metals, iron, cobalt, and nickel belong to the first horizontal triad of Group VIII of the periodic table. The atoms of these metals contain respectively 8, 9, and 10 outer electrons. The most stable oxidation state of cobalt and nickel is 2+, although cobalt is often trivalent as well in coordination compounds such as $Co(NH)_3Cl_3$. The metals resemble each other in chemical behavior, with similar densities and high melting points, though of the two nickel is more commonly used in industrial applications. There are two reasons for this; first, nickel is about four times more abundant than cobalt, and second and more important, nickel is more easily protected against corrosion.

Although quite similar to cobalt and nickel, iron is much more widely used. (Iron is discussed in a separate article.) Cobalt and nickel are treated together because of their great similarity.

COBALT ORES; EXTRACTION AND PROPERTIES OF THE METAL

Though not widely distributed in the rocks of the earth's crust, cobalt is always found with ores of nickel (the ratio is 1:15) and sometimes with ores of copper. It is commonly combined with arsenic and sulfur as well. This makes extraction easy, with cobalt being obtained as a by-product of the processing of arsenic and sulfur, which are more widely distributed and more abundant in nature than cobalt itself.

Cobalt also occurs in siderites (meteorites composed chiefly of iron) where its ratio with respect to nickel is a little higher than in the earth's crust.

Cobalt-bearing ores include smaltite ($CoAs_2$, a cobalt arsenide) and cobaltite (cobalt arsenic sulfide $CoAsS$). Countries with the largest production of cobalt are the Republic of the Congo and Canada, where it is found associated with nickel.

World production of the metal is at present little more than 10 thousand tons a year, although this figure is rising as a result of heavy demand from the special alloys industry. Cobalt is also extracted during the refining of copper, where it is an impurity. The pure metal can be obtained by electrolysis also.

Cobalt is a silver-white, brittle metal that is magnetic (though less so than iron) and chemically resistant to air. The only acid capable of corroding it readily

$NiSO_4$—Nickel sulfate, enlarged 100 X and seen under red polarized light.

is nitric acid. When treated with nitric acid it forms cobalt(II) nitrate.

CHEMICAL PROPERTIES AND COMPOUNDS

Cobalt behaves either as a bivalent or trivalent metal, combining with oxygen to form cobalt(II) oxide, CoO, or cobalt (III) oxide, Co_2O_3 (there is a tetravalent form, but it is unstable and of little importance). Cobalt(II) oxide, CoO, is almost insoluble whereas cobalt(III) oxide Co_2O_3 is almost completely soluble. Thus, salts of cobalt are usually prepared by synthesis of the elements or by the action of acids on the metal. Dissolving cobalt in

STAINED GLASS WINDOW IN MILAN CATHEDRAL—The various shades of blue are caused by small quantities of blue cobalt oxide that neutralize the yellow tinge given to the glass by iron.

hydrochloric acid, for example, produces the salt of cobalt(II), colbalt(II) chloride, $CoCl_2$, which is a rose-red color in the hydrated state and bright blue in the anhydrous state.

The sulfate, $CoSO_4 \cdot 6H_2O$, chloride, $CoCl_2 \cdot 6H_2O$, and nitrate, $Cl(NO_3)_2 \cdot 6H_2O$ are the most common salts of bivalent cobalt. These salts are all soluble in water. Cobalt(II) sulfide, CoS, on the other hand, is insoluble. Salts of trivalent cobalt are more difficult to produce. The sulfate, $Co_2(SO_4)_3 \cdot 18H_2O$, which is obtained by anodic oxidation of sulfuric acid solutions of bivalent cobalt salts, is unstable. Complexes of trivalent cobalt, on the other hand, are very stable.

The chief cobalt(II) compounds are the chloride, sulfate, nitrate, cyanide, and ammoniate, while the chief cobalt(III) compounds are the hydroxide, fluoride, nitrate, and various types of mixed sulfates of cobalt and other elements. Complex ions of cobalt(III) are also quite important.

SUPERHARD ALLOYS, CERAMICS, PIGMENTS

Cobalt is put to many uses, both in the manufacture of special alloys and as a pigment. Some of the alloys are of special importance.

Widia is an alloy consisting of 90 percent tungsten carbide W_2C and the rest cobalt. Used to make metal-cutting tools, it is extremely hard (its name means "like diamond"), can cut glass, and can be used at high temperatures without losing its edge. It is resistant to oxidation.

Stellite is an alloy of cobalt, chromium, and tungsten. Also very hard, though less so than widia, it is used for tools, for cutting and working metals, for dies, presses, shears, and also, because of its corrosion resistance, for chemical apparatus. Another application is in the field of optics, where it is used to make special mirror surfaces. These mirrors are used in apparatus where radiation from radioactive elements is high.

Gas and steam turbine blades are also made from a variety of high-cobalt alloys. The cobalt gives the blades hardness as well as resistance to heat and corrosion.

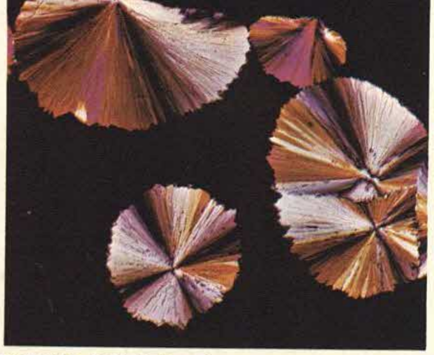
Many cobalt salts are blue in color, and when added to pottery or glass, produce a characteristic bright blue color known as Sèvres blue, Thenard's blue, or simply cobalt blue.

Cobalt(II) chloride, $CoCl_2$, is blue in

color when anhydrous and pink when hydrated. It is sometimes used in solution as invisible ink. When the solution dries, the hydrated salt deposited on the paper is almost colorless and hence invisible. When the paper is heated, however, the salt loses its water of hydration and turns bright blue.

Cobalt has only one stable isotope, ^{59}Co. When bombarded with slow neutrons in a nuclear reactor, it captures a neutron and emits a gamma ray, turning into ^{60}Co. This radioactive isotope is used in radiotherapy.

Isolated by the Swedish chemist Georg Brandt in 1735, cobalt owes its name to Kobold, a gnome of German folklore thought to inhabit underground places.



COBALT ACETATE—These beautifully colored shavings are microcrystals of one of the compounds of cobalt. They are enlarged 100 X and seen under red polarized light.

NICKEL ORES, EXTRACTION, AND PROPERTIES

Nickel was isolated by the Swedish chemist Axel F. Cronstedt in 1751 and probably gets its name from the Swedish word *kopparnickel*, itself a translation of the German *kupfernickel* or "copper demon." Nickel ores occur in a number of rocks. Economic extraction, however, is restricted to a few localities, despite the considerable value of the metal. The chief source of nickel is the Sudbury deposits in Canada, which account for over half the world production. Other deposits of some importance are in New Caledonia, Lapland, and Cuba.

Nickel ores include millerite (nickel sulfide), niccolite (nickel arsenide), gersdorffite (nickel sulfarsenide), garnierite (hydrated nickel magnesium silicate), and pentlandite (nickel iron sulfide).

Extraction processes differ in terms of the ore used. The usual procedure is to produce a nickel sulfide (nickel has a strong affinity for sulfur), which is then heated in the presence of air (roasting) to produce nickel oxide. The oxide is then reduced to the metal with carbon.

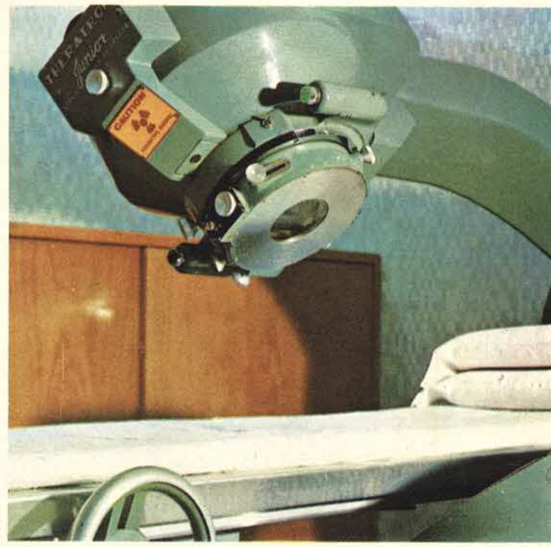
Metallic nickel is a pure white in color, with no yellowish or bluish tinges. It is strong, ductile, malleable, reasonably conductive (its conductivity is about one seventh of that of copper), resistant to oxidation when cold, and resistant to all acids except concentrated nitric acid. When finely powdered, it absorbs large quantities of hydrogen, and is thus used as a catalyst in hydrogenation reactions and in fat-hardening processes.

NICKEL COMPOUNDS AND USES

Nickel usually behaves as a bivalent element. The univalent, trivalent, or tetravalent states are rare. Nickel compounds, which have no important applications, include nickel oxide NiO; the gelatinous light green nickel hydroxide $Ni(OH)_2$; nickel carbonate $NiCO_3$ and nickel sulfide NiS (both insoluble salts; NiS is produced by treating solutions of salts of nickel with hydrogen sulfide in the presence of an alkali); nickel sulfate $NiSO_4 \cdot 6H_2O$, nickel chloride $NiCl_2 \cdot 6H_2O$, and nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (all green in color and soluble).

NICKEL-TREATED GRAY GLASS—The characteristic gray color of this goblet is caused by the addition of nickel (II) oxide for scientific or decorative reasons.

Nickel oxide is used to impart a gray color to glass for scientific and decorative purposes. Nickel itself is most commonly used in the elementary state or in alloys. One use of nickel in the elementary state is nickel-plating, in which a layer of nickel is deposited on the surface of other metals to protect them from corrosion. The metals most frequently plated are iron, copper, and copper alloys. Nickel-plating is done by electrolysis and has certain advantages over chromium-plating, particularly when the nickel is applied in thick layers. Its bond is not weakened even when the metal underneath buckles, whereas chromium, being brittle, may split and expose the metal to oxidation.



COBALT THERAPY—Used to treat cancer, the radiation from cobalt-60 burns out cancerous cells and prevents their growth.

Although chromium-plating is cheaper, nickel-plating remains a better form of protection for high-quality work.

Nickel is also used, together with chromium and iron, to make the alloy known as stainless steel, whose high resistance to corrosion by many agents, whether hot or cold, makes it highly suitable for structural work. Alloyed with copper and copper-zinc alloys, nickel is also used to make coins, kitchen utensils, and parts of heat engines that are vulnerable to corrosion. Alloyed with copper, chromium, and molybdenum, it is used to make electrical resistors and corrosion-proof apparatus. Many types of alloy steel contain nickel as an ingredient.

The chief alloys of nickel include constantan (60 percent copper and 40 percent nickel); invar, an iron alloy with 35 percent nickel; and alnico, named for its chief constituents—aluminum, nickel, and cobalt.

PHOSPHORUS | soft water, strong bones, and fertile soil

Phosphorus (P) is one of the most widespread of the elements, accounting for 0.1 percent of the Earth's crust. Although this element is never found in the native state, it is present in combined forms in about 250 different minerals. The most important of these is apatite, a phosphate-containing mineral found in a variety of forms. In fact, most apatites are isomorphous mixtures containing primary calcium phosphate in association with calcium fluoride, chloride, and hydroxide. Because of their similar electron charges and atomic diameters, these three ions are able to alternate or replace one another in the same crystal lattice without appreciably changing it.

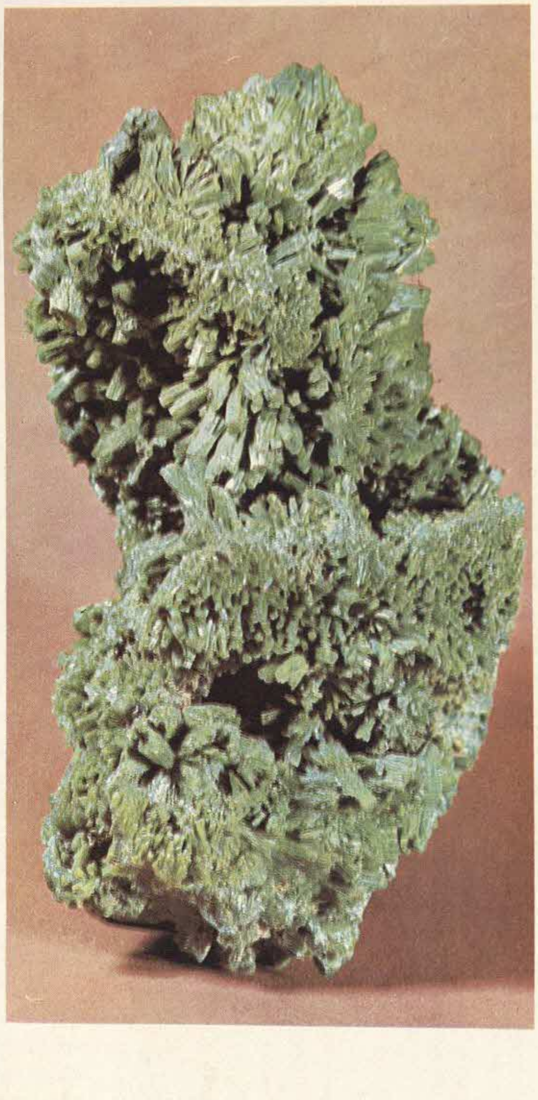
Apatite crystals are formed during the solidification of volcanic magmas, and because of their insolubility remain essentially unaltered by subsequent erosion and weathering. However, the rock in which they are formed is changed by natural forces into sedimentary rock and finally into sand. Thus, the crystals find their way into the soil where they are essential to healthy plant growth. Where nature falls short, man intervenes by adding phosphate fertilizers derived from rich apatite deposits or other natural sources.

APATITE—Industrially the most important of the phosphorus ores, apatite's crystals are nearly always perfectly prismatic and hexagonal.

1

PYROMORPHITE—This beautiful earthy-green mineral forms colorful prisms, and has the formula $Pb_5Cl(PO_4)_3$. It is frequently found in lead mines.

2

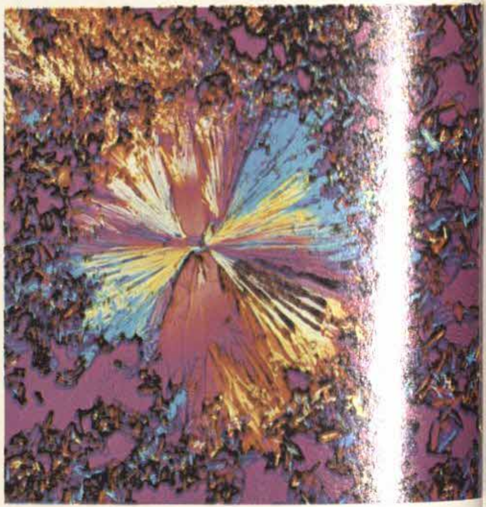


PHOSPHORUS, ANIMALS, AND MAN

Not only is phosphorus essential to vigorous plant growth—it is also a prerequisite for healthy animal life. Fortunately, the biological cycle supplies most of the phosphorus required by man.

Phosphorus is found in cell protoplasm, in bone and nerve tissue, and in many animal and vegetable proteins. Except for its organic components, bone tissue consists of phosphate compounds not at

3a



all dissimilar to natural apatites, while tooth enamel has a chemical composition much like fluorapatite.

Although phosphorus is an essential ingredient in the diets of man and the lower animals, not all of this element is used by the organism. Thus, much of what is ingested is eliminated, explaining why animal wastes are rich sources of phosphorus, and indeed are used to replenish the soil as fertilizers.

Pharmacologically, a distinction exists

between phosphorus compounds containing oxygen and those without oxygen. First, both types can be highly toxic. However, one of the nonoxygenated compounds, phosphine, deserves special mention. Phosphine, PH_3, is a highly lethal gas that can cause death in concentrations as low as 0.01 percent in air. This substance reacts with arterial blood to reduce the hemoglobin, the phosphine being oxidized to phosphoric acid. The twofold effect is to destroy the oxygen-carrying ability of the blood and to create a severe acid-base imbalance. Fortunately, phosphine can be detected by its intense, nauseating odor, similar to that of decaying fish.

All of the oxides of phosphorus are toxic substances, and are formed by direct synthesis. In fact, elemental yellow (or white) phosphorus burns spontaneously on contact with air, evolving clouds of white, poisonous gas. White phosphorus is used in warfare in the production of incendiary bombs and for the generation of smoke screens.

Certain oxygenated derivatives, on the other hand, are vital to human life. One of the most important of these is, strangely enough, phosphoric acid (although in amounts considerably less than encountered through phosphine poisoning). Phosphoric acid forms in the process of digestion, and plays a fundamental role in the metabolism of sugars. This process, called phosphorylation, is the first step in breaking down monosaccharides. This reaction is exothermic, thus providing the body with both heat and energy. Despite this life-sustaining function, most phosphorus derivatives are incorporated into bone, muscle, and nerve tissue.

3b

HIDDEN BEAUTY—Illustration 3a shows crystals of normally white dibasic sodium phosphate under polarized light. The brilliant "gems" in Illustration 3b are really a common salt, potassium phosphate. In polarized light, this white compound becomes jewel-like.

DEPOSITS OF PHOSPHORUS ORES

Phosphorus ores are found in the southeastern United States, Canada, Spain, the Soviet Union, and all the countries of North Africa. Many islands in the Pacific Ocean are almost totally covered with thick deposits of guano, the natural wastes of seabirds. Guano is particularly rich in phosphates, and although the world supply of this biological material is dwindling because of demand, it is still widely used as fertilizer.

THE PROPERTIES OF PHOSPHORUS

Phosphorus was first isolated by the German chemist Hennig Brand in 1669. He obtained a small quantity of the element following evaporation of urine and heating of the residue with sand and charcoal in the absence of air. Since phosphorus glows faintly when exposed to the air at low temperatures—a property called phosphorescence—the name of the element was derived from the Greek term for "light-bearing." Brand did not disclose his method of producing phosphorus, but he sold the secret to Johann Krafft of Dresden. The chemist Johann Kunckel sought to learn the method from Brand but learned only that urine was used as the source of the phosphorus. Eventually he was able to duplicate

WHITE PHOSPHORUS — In the pure state, phosphorus is almost colorless. Because it ignites spontaneously in air, it is stored underwater.

4

5

RED PHOSPHORUS—The most stable of the three phosphorus allotropes, red phosphorus is a product of the transformation of white phosphorus.

Brand's accomplishment, and Kunckel, too, attempted to keep the process a secret. In the decades that followed, methods were developed—and, in some instances, published—for preparing phosphorus from various animal and vegetable materials. It was more than a century, though, before the Swedish chemist Carl Scheele published the simpler method of preparing the element from bones, which were to become the main raw material to be used as a source of phosphorus. Today, phosphorus is obtained in commercial quantities by heating phosphate rock with sand and carbon in an electric furnace:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + \tfrac{1}{2}P_4.$$

Depending on atomic and molecular arrangement, phosphorus occurs in three allotropic forms: white (or yellow), red, and black (or violet). At ordinary temperatures, white phosphorus is a soft, translucent substance that reacts with air to form the pentoxide. At decreased temperatures, this form becomes quite brittle. White phosphorus boils at 280° C (536° F), and at a point between 500° and 800° C (932° and 1,472° F), the vapor is composed entirely of tetratomic P_4 molecules. Continued heating to highly elevated temperatures causes these molecules to collide violently, splitting them into diatomic P_2 molecules and perhaps even to monatomic P atoms.

Although it is the most common form of the element, white phosphorus is the least stable of the allotropes, igniting spontaneously in air at room temperature and reacting explosively with the halogens. In alkaline solutions, it forms the phosphite ion $(PO_2)^{3-}$ and phosphine.

The most stable form of phosphorus is the red allotrope. It is formed from the white variety under pressure and sustained heat. In the process, a considerable amount of heat is liberated due to the creation of polymeric molecules. Though less toxic and reactive than the white form, red phosphorus can be reconverted to the white state.

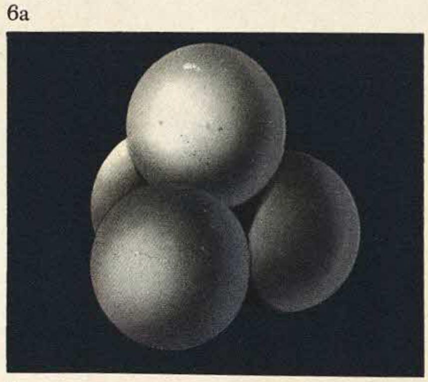
Black phosphorus is the third allotrope of the element, and can be made by heating white phosphorus under high pressure. Sometimes called violet phosphorus, black phosphorus is the most dense of the three types.

Chemically, phosphorus is a member of the Group VA family of elements—the group's most ubiquitous member, in fact. The atoms of phosphorus are characterized by having five electrons in the outer shell, giving rise to valences from −3 to +5. Typically, however, only those oxidation states of −3, +3, and +5 are encountered, as in PH_3, PCl_3, and P_2O_5, respectively.

Phosphorus—in particular the white

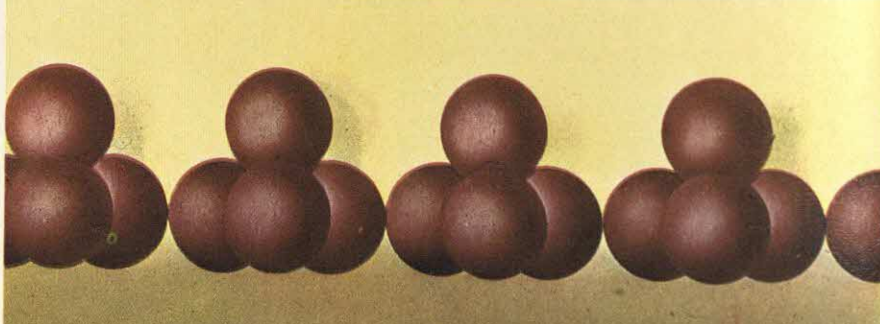
THE THREE FORMS OF PHOSPHORUS—The model in Illustration 6a represents a molecule of white phosphorus, with its four atoms arranged in a tetrahedron. The black modification in Illustration 6b is also arranged tetrahedrally, but probably forms a polymeric chain. Red phosphorus (Illustration 6c) is a true polymer.

6a



6b

6c



form—shows a strong affinity for almost all elements. With oxygen, for example, it forms at least four oxides. The element is also an energetic reducing agent.

PHOSPHORUS COMPOUNDS

Phosphorus forms many compounds with oxygen, not only in single combination, but in association with oxygen and other elements. The phosphorus oxides all have the character of acid anhydrides, and the acids they form with water have varying degrees of strength. Of the oxides, the most important are the trivalent P_2O_3 (phosphorous anhydride) and the pentavalent P_2O_5 (phosphoric anhydride). Another oxide, phosphorus tetroxide (P_2O_4), is composed of an atom each of +3 and +5 phosphorus. Together, the phosphoric and phosphorous ions form a total of 9 acids, some quite strong.

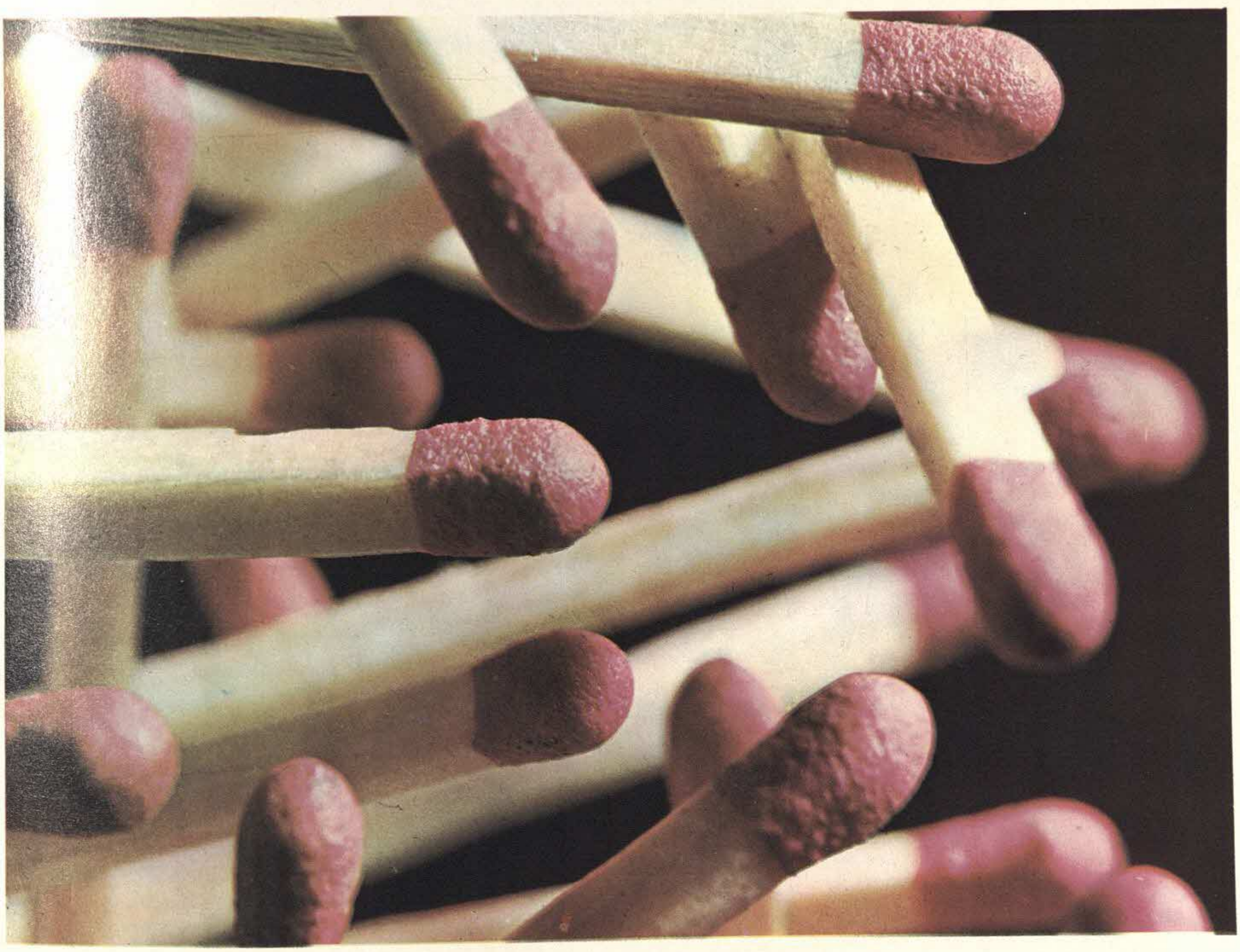
Phosphorus pentoxide reacts vigorously with water, and is one of chemistry's most energetic dehydrators. From its acids are derived the invaluable soluble phosphate fertilizers. In addition to their value as fertilizers, certain +5 phosphorus compounds are efficient and relatively inexpensive water softeners. Of these, sodium hexametaphosphate is used to prevent scale formation in boilers and hot water pipes. This is accomplished by the ion's ability to capture calcium in hard water, keeping it in solution and preventing the precipitation of calcium carbonate scale.

Because of their water-softening properties, phosphates have long been used in detergents. Recently, however, controversy about these compounds and their contribution to water pollution has led to research into and production of other materials having less damaging ecological effects.

Halogenated phosphorus compounds form a large group, the most important of which are the chlorides. Phosphorus and chlorine combine directly—and violently—to form phosphorus trichloride. This is the starting point for a host of chlorinated compounds. Of these, the pentachloride is of special importance in organic synthesis, where it replaces OH radicals in many compounds with Cl^- ions, making it a very effective chlorinator.

7

A FOREST OF PHOSPHORUS—Red phosphorus is shown here in one of its most common applications—ordinary matches. The highly poisonous and unpredictable white phosphorus was once used in this manner, but it is no longer.



VANADIUM | the soft metal that hardens steel

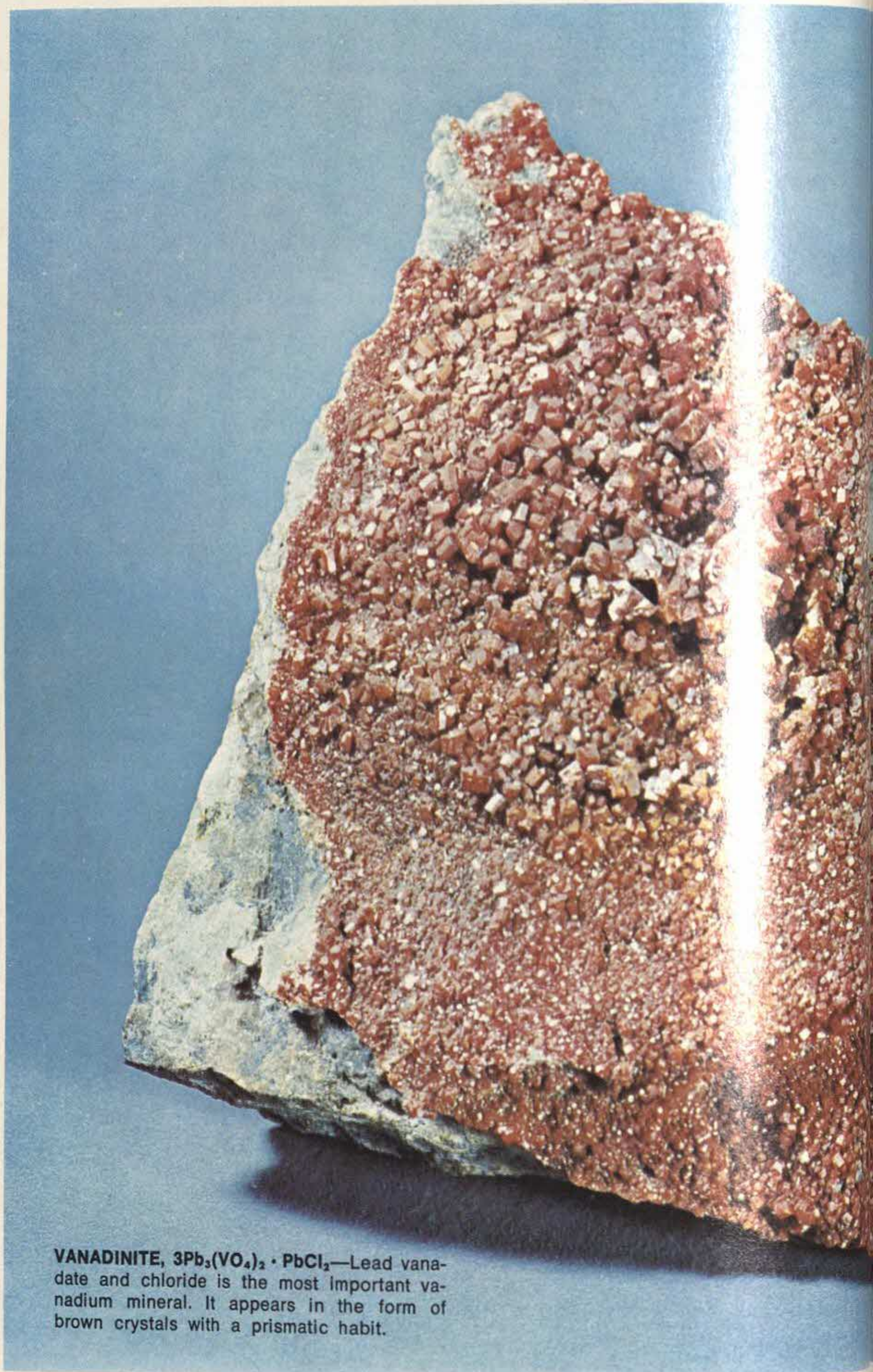
Vanadium (V) belongs to Group VB of the periodic system, along with niobium and tantalum. Its normal oxidation state is +5, but it can also take lower oxidation states, as with niobium and tantalum. However, this tendency decreases as atomic weight increases, so that although it is true that vanadium may easily take all the valencies from +2 to +5, niobium and tantalum are immediately oxidized by water in the lower states. These last two elements are metallic in nature and crystallize with a body-centered cubic structure.

Metals of Group VB are sometimes harder and more brittle than is desirable because they contain very small quantities of hydrides, nitrides, and carbides, which alter the properties of the metal itself. The approximate chemical formula of hydride, nitride, and carbide of vanadium is VH, VN, and VC, respectively. The formulas are approximate because these compounds are of the interstitial type; that is, hydrogen, nitrogen, and carbon occupy some of the interstices left free in the metal's crystal lattice.

The specific gravity of vanadium, niobium, and tantalum increases with increasing atomic weight. This is explained by the fact that the increase in weight means an increase in the protons in the nucleus and, consequently, in the electrons as well. This increase in the positive charge of the nucleus makes it more capable of attracting electrons toward the nucleus. Consequently, the atom is more compact and the density of the solid is greater. The density increases from 5.96 g/cm^3 for vanadium to 8.55 g/cm^3 for niobium and to 16.6 g/cm^3 for tantalum.

Melting points increase with increasing atomic number and range from 1,890° C to 2,468° C, and 2,996° C (3,434° F, 4,774° F, and 5,424° F) for vanadium, niobium, and tantalum, respectively. The melting point of tantalum makes it the second most refractory of all the elements (tungsten is the first). The boiling point also increases with increasing atomic number, that is, Z.

1



VANADINITE, $3Pb_3(VO_4)_2 \cdot PbCl_2$—Lead vanadate and chloride is the most important vanadium mineral. It appears in the form of brown crystals with a prismatic habit.

VANADIUM, A RELATIVELY ABUNDANT METAL

Vanadium is relatively abundant in the lithosphere, which contains about 150 g per metric ton of rock. It is much less abundant, however, than iron and aluminum (50 and 80 kg per metric ton). On

the other hand, it is 6 and 70 times more abundant, respectively, than the homologous elements niobium and tantalum.

The minerals of vanadium are numerous. They are contained in almost all eruptive rocks and many of them are found in sedimentary rocks as well. The major minerals are: carnotite—potassium uranyl vanadate; descloizite—hydroxyvanadate of lead, tin, and copper; mottramite, with a chemical composition almost identical with descloizite, but with a slightly different structure; vanadinite—lead vanadate and chloride $3Pb_3(VO_4)_2 \cdot PbCl_2$; volborthite—hydrous vanadate of copper; and patronite—vanadium sulfide, VS_4.

Many hydrated vanadates are also known, in particular uranyl vanadate. They are used in the extraction of uranium, and vanadium itself is obtained as a by-product—especially from the use of carnotite.

Vanadinite and patronite are important vanadium minerals. Vanadinite is found in Arizona and patronite in Peru. Vanadium is also found in the animal and plant world. Although its location within organisms is still not known with any accuracy, it has been found in the ashes of certain plants and the body fluids of certain holothurian marine animals. Appreciable quantities of vanadium are also found in the form of organic complexes in certain petroleums, especially those of Venezuela. Vanadium becomes concentrated in the residues resulting from distillation, and further concentrated in the ashes of these residues when they are burned. For those who subscribe to the theory that petroleum has a biological origin, it may be said that the vanadium contained in "black gold" came from the structures of the living beings that gave rise to it.

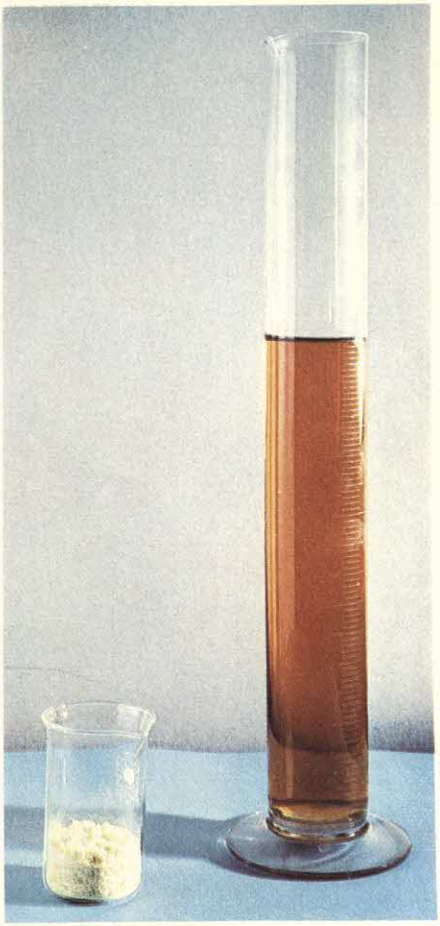
THE DISCOVERY OF VANADIUM

At the beginning of the last century chemists did not know how to separate from steel those elements present in iron minerals in small quantities—elements that then reappear in the metal produced in the blast furnace. Because the iron minerals found in Sweden are especially rich in these elements, the steels produced there often had peculiar properties, some of which were desirable and some of which were not.

In 1830, the Swedish chemist Nils Gabriel Sefström, who was working in the laboratory of J. J. Berzelius in Stockholm, analyzed the toughness properties of a certain steel. Despite the fact that it was extremely resistant—as resistant as the ordinary brittle steels—the steel was as malleable as ordinary iron. This property evidently came from an element that Sefström decided to isolate. Although he was not successful, he was able to show that this still unknown element existed and he gave it the name of a Scandina-

2

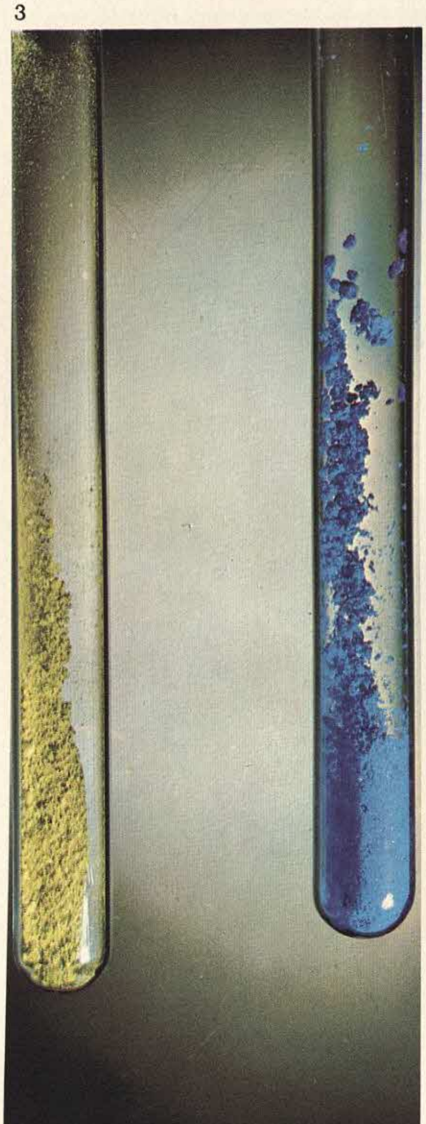
TETRAVANADATE AND PERVANADATE— Sodium tetravanadate has a yellowish color. An acid solution of it to which hydrogen peroxide is added rapidly becomes reddish-brown. A pervanadate has been formed in which the vanadium has changed its oxidation state and is more oxidized.



vian goddess, Vanadis. A quarter of a century earlier, Andres Manuel del Rio reported the discovery of a new element in vanadinite from Zimapán, Mexico. He named it erythronium (from the Greek word for "to redden") because of the red color acquired by its salts upon heating. A few years later he concluded that he was mistaken and that the brown ore from Zimapán was merely a basic lead chromate. Before Sefström's discovery, the German chemist Friedrich Wöhler had undertaken an examination of the vanadinite ore from Zimapán, and he

VANADIUM SALTS—The vanadyl sulfate tetrahydrate $VO \cdot SO_4 \cdot 4H_2O$ is intensely blue. Vanadium sulfate, VSO_4, on the other hand, is yellow.

3



found in 1830 that the new element Del Rio had abandoned was identical to Sefström's vanadium. Because of illness, Wöhler failed to report his findings and thus did not receive credit for discovering this new element. In 1831 Berzelius prepared a number of vanadium compounds and concluded that the element belonged in the same family as chromium and molybdenum. The English chemist Henry E. Roscoe showed, between 1867 and 1870, that Berzelius was wrong in his conclusion because the substance that Berzelius had assumed to be the free metal was really the oxide, VO, and that, therefore, most of the compounds studied by Berzelius had contained oxygen. Roscoe was the first (1869) to obtain the pure metal (95.8 percent) by reduction of vanadous chloride, VCl_2, with hydrogen. Metallic vanadium has been hard to isolate in a highly pure state because of the great stability of its lowest oxide, its nitride, and its carbide. Eventually, metallic vanadium 99.7 percent pure was obtained by heating a mixture of vanadium pentoxide, calcium metal, and calcium chloride for one hour at 900 to 950° C (1,652 to 1,742° F). Pure vanadium was being produced in limited quantities by the mid-twentieth century.

THE PRODUCTION OF THE METAL

The United States is the world's largest producer of vanadium, and uses it in the manufacture of steels with special properties. Vanadium is obtained in its metallic state by the process of reduction —the variation of the element's oxidation state by the acquisition of electrons. This involves transforming the vanadium present in the original mineral (such as bitumen ash) into a chloride or oxide of vanadium, and thence into the metal itself.

This is done in various ways. One way is to pass a high-temperature current of hydrogen gas over vanadium chlorides or oxides. Metallic calcium may also be used to remove the oxygen from vanadium oxide. Hydrogen and calcium have such an affinity for oxygen that they remove it from the vanadium oxide. This process is also used for reducing uranium from the metal oxide. The reaction in the case of calcium is as follows:

4

IRON-VANADIUM ALLOY—Adding vanadium or ferrovanadium to steel makes it harder and more resistant to corrosion, eliminating the gases that may be trapped in it.

$$V_2O_5 + 5Ca \rightarrow 2V + 5CaO.$$

Pure vanadium is rather soft—as are most metals in their pure state. Vanadium, lead, and tin are about equally hard. When added to steel, however, vanadium increases the hardness of the alloy. An extremely small amount is enough to do this—only a few thousandths (by weight) of the resulting alloy.

The fact that a soft metal added to another metal makes it harder may be surprising—but it is a common phenomenon. Tin, for example, which is soft, makes copper hard in alloys called bronzes. (The type of bronze varies according to the percentage of its constituents.) To understand the phenomenon, the way in which the vanadium atoms are arranged among the iron atoms in the crystal lattice of the alloy must be understood. However, it is sufficient to know that each time vanadium atoms are introduced into the crystal lattice of another metal, they modify the forces in the lattice that act on the atoms and bind them together. This phenomenon becomes translated into a variation in the physical properties of the metal—its hardness, malleability, and so forth. Vanadium added to iron increases its toughness and hardness.

The vanadium to be introduced into an alloy with iron is usually prepared from the oxide by using the process known as aluminothermy. This process consists of

reducing the vanadium oxide by means of aluminum, which is extremely oxygen-hungry, and which is mixed with the iron oxide. The aluminum reduces both the vanadium oxide and the iron oxide. The result is an iron alloy that is rich in vanadium (about 30 percent). This is introduced into the iron to form alloys with a lower percentage content (0.2 percent). In steels, vanadium also has the function of eliminating occluded gases in the metal mass. These gases are detrimental to the properties of the metal.

CHEMICAL PROPERTIES AND COMPOUNDS

In addition to the +5 valence with which it is linked to oxygen in vanadium pentoxide, V_2O_5, vanadium also has valences of +4, +3, and +2.

Vanadium pentoxide has various applications. It is an energetic catalyzer of the reaction in which sulfur dioxide is oxidized to sulfur trioxide in the manufacture of sulfuric acid. It also catalyzes many other oxidation reactions and is, therefore, used extensively in the chemical industry, which is the second largest consumer of vanadium pentoxide. (The special steels industry is the largest consumer.)

Many compounds deriving from vanadium pentoxide are known, such as the various acids and corresponding salts. The alkaline vanadates, such as $Na_3VO_4 \cdot H_2O$, give rise to solutions containing thiovanadates ($MeVS_4$) when reacted with hydrogen sulfide, H_2S. They are intensely colored, and the colors range from a cherry red to a violet red. The most important thiovanadate is $(NH_4)_3VS_4$.

The salts of the simple vanadic acids are colorless. Those of the more complex vanadic acids, on the other hand, are yellow or orange. All the vanadium compounds in which the element has a valence of less than 5 are colored: vanadium dioxide, VO_2, is dark blue; vanadyl chloride, $VOCl_2$, is dark green; the trivalent ion of vanadium has a greenish color in solution; the hydroxide, $V(OH)_3$, is green; the alum of cesium and vanadium, $Cs_2SO_4 \cdot V_2(SO_4)_3 \cdot 24H_2O$, is bluish purple; the sulfide, V_2S_3, is dark gray; the hydroxide, $V(OH)_2$, is dark brown; and the sulfate, $VSO_4 \cdot 7H_2O$, is reddish purple.

In vanadium sulfate, $VSO_4 \cdot 7H_2O$, the electrons of the molecule absorb green light. White light passing through it, therefore, has the green removed and only the complementary color—the color obtained by adding those remaining in the spectrum—is left. This color is reddish purple.

VANADIUM—This specimen shows the characteristic shininess of vanadium. At its purest, vanadium is almost as soft as lead.

ALUMINUM | the corrosion-proof competitor of iron

Aluminum (Al) belongs to Group IIIA of the periodic table of the elements, along with boron, gallium, indium, and thallium. In its compounds, aluminum occurs exclusively in the oxidation state of +3. Aluminum is a silvery-white metal easily corroded by nonoxidizing acids, resulting in hydrogen (since it is an electropositive metal), and by alkalis. In reaction with alkalis, aluminum forms various hydroxylaluminates according to the following reaction:

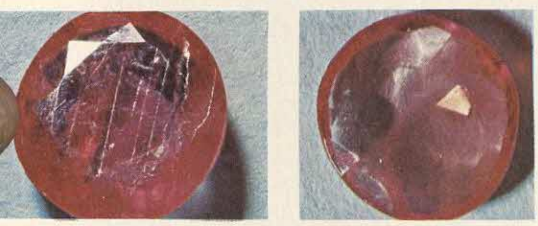
$$Al + NaOH + 2H_2O \rightarrow NaAl(OH)_4 + \frac{3}{2}H_2.$$

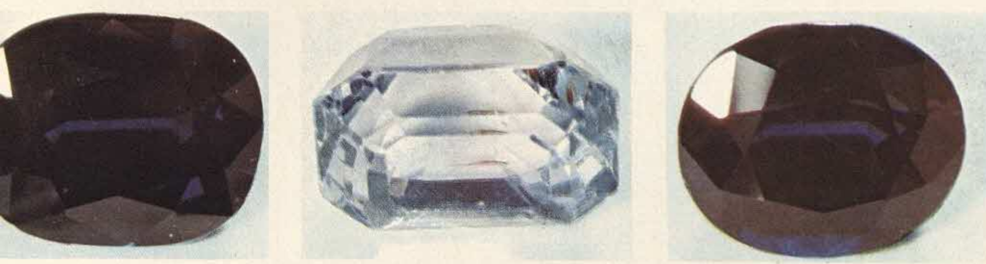
Oxidizing acids, such as nitric acid, corrode aluminum only superficially because a film of aluminum oxide, Al_2O_3, forms on the surface of the metal, protecting it from further corrosion. This phenomenon is called passivation.

Aluminum takes third place in the list of the most widely distributed elements in the Earth's crust; it is exceeded only by oxygen and silicon, and is the most abundant of the metals (8.3 percent). Although the extraction of aluminum is not always economically feasible, it is found in a great variety of rocks and the world supply is virtually inexhaustible.

The history of aluminum begins in 1825, when Hans Christian Oersted, the Danish physicist, first succeeded in obtaining the metal in its elementary state, although full of impurities. Two years later the German chemist Friedrich Wöhler obtained a much purer product. These events went almost unnoticed except for the recognition that a new element had been isolated and that it was quite expensive. At such a price, aluminum was among the precious metals, and although no special use was found for it, aluminum was used to cast the cap of the Washington Monument. When it was finally put to industrial use, and production techniques had improved, the price came down rapidly.

1





RUBIES AND SAPPHIRES—The best-known and highest-valued compounds of aluminum are rubies and sapphires. Rubies are a beautiful red color and flawless specimens may be worth even more than diamonds. Two magnificent Oriental rubies are shown on the left. Below are three variously tinted sapphires: the two deep-blue sapphires were mined in Burma, and the lighter one in the center comes from Ceylon. The characteristic coloring (which gives the stones their value) is due to traces of other metals or faults in the crystal lattice.

2

SYNTHETIC RUBIES AND SAPPHIRES—Like diamonds, rubies and sapphires can be synthesized in crystals for use in jewelry and industry. Pure specimens of synthetic ruby are used to make pulse laser rods and precision instruments. Transparent sapphires (left, also called pure corundum) are used to make windows for infrared optical equipment.

ALUMINUM ORES

Because of its high reactivity, aluminum is not found in the natural state, but is combined with either larger or smaller amounts of oxygen in the form of oxides. It also occurs as hydrates and as silicates of somewhat complex composition.

Compounds in which silicon atoms are partially replaced by aluminum atoms are known as aluminum silicates and include nepheline, $Na(AlSiO_4)$, anorthite, $Ca(AlSiO_4)_2$, leucite, $K(AlSi_2O_6)$, and orthoclase, $K(AlSi_3O_8)$.

Another extremely stable and hard compound is the aluminum oxide, Al_2O_3, known as corundum. Normally occurring in nature in its transparent form, the colored varieties of corundum are caused by the presence of impurities of various metals. Traces of cobalt, for example, produce the precious sapphire and aquamarine, while chromium impurities turn corundum into ruby. The value of these gems is in direct proportion to their clarity and the intensity of their coloring. The value of a fine specimen of a ruby is not far short of that of a diamond. When crystallized in large masses with iron oxide, Fe_3O_4, this oxide is also extracted and used as an abrasive, in which case it is given the name of emery; it is only slightly less hard than the hardest of all synthetic abrasives, silicon carbide.

The cheapest of the aluminum ores is bauxite, a hydrate with the formula $Al_2O_3 \cdot 2H_2O$. (The formula is not completely accurate in that the mineral consists of a mixture of more or less hydrated oxide molecules.)

Another ore used in aluminum extraction is cryolite, a double sodium aluminum fluoride, $AlF_3 \cdot 3NaF$; but these ores account for only a small part of the aluminum found in the lithosphere. Cryo-

3

WORLD DISTRIBUTION OF ALUMINUM—Included in the composition of a large number of rocks, aluminum is widely distributed in the lithosphere. This does not mean that it can always be extracted economically, but aluminum ore reserves are so large as to be almost inexhaustible. The triangles on the map mark the locations of the richest deposits of bauxite, the most economically feasible aluminum ore.

lite is especially widely distributed in feldspars and micas, which (together with quartz) are found in large quantities in eruptive rocks. Cryolite also occurs in sedimentary rocks, specifically in minerals formed by the disintegration of eruptive rock. Chief among these are kaolins (formed by the breaking up of feldspars) and clays.

Extracting aluminum from bauxite and cryolite is a highly complex industrial process. The first step is the electrolysis of a mixture of alumina and natural or synthetic cryolite. The cost of aluminum thus depends to a great extent on the cost of the electric power required to produce it.

PURE ALUMINUM

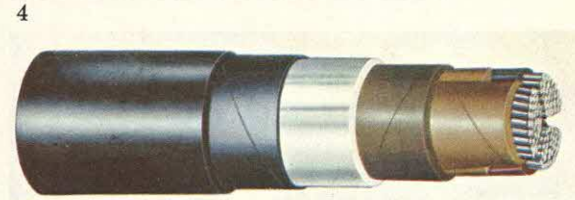
The electrolytic method of processing aluminum yields a high degree of purity. A metal 99.5 percent pure is normal and may reach 99.9 percent if it is first partially refined and then repeatedly electrolyzed. Such purity is a necessary condition if the metal is to come into contact with foodstuffs. Pure aluminum has exceptional properties. As a conductor of electricity it is inferior only to silver and copper and is widely used in the manufacture of electric cables for high-tension lines because of its lower weight compared to the other two more conductive metals.

The only disadvantage of pure aluminum is that it is quite weak mechanically. Pure aluminum cables would bend and eventually break under the action of the wind; to prevent this, such cables are alloyed with other metals for strength and are usually provided with a core of steel wire.

The thermal conductivity of pure aluminum is also very high, although inferior to that of copper and silver. These two properties, electric and thermal conductivity, are found together because they both depend on the mobility of the electrons in the crystal lattice. As regards crystallization, aluminum belongs to the category in which the atoms are arranged in a face-centered cubic lattice.

The specific gravity of aluminum is 2.70, which makes it a very light metal and therefore suitable for use in a variety of products, including aircraft parts, especially when alloyed with other metals. It also has a fairly low melting point—

4



TRIPOLAR CABLE—This power cable consists of aluminum conductors insulated with specially treated paper and housed in an aluminum tube protected by a plastic sheath.

659.7° C (about 1,220° F)— making fabrication techniques simple and costs low.

Aluminum's property of oxidizing very readily protects it from corrosion by atmospheric agents, in that the coating of oxide that forms rapidly on the surface of the metal is extremely hard and resistant to most atmospheric corrosive agents. This film of oxide can also be produced electrolytically and need only be a few thousandths of a millimeter thick to protect the metal adequately. In the building industry, where aluminum is used to face external parts, the coating of oxide may be as little as 10–15 μm thick and may be applied in a vast range of color by the use of colored additives. Because the coating is made electrolytically with aluminum as the anode, this process is called anodization.

Pure aluminum is less liable to corrode than its alloys, the commonest of which are made by adding magnesium, silicon, copper, or manganese to the pure metal. Duralumin, for example, contains 3 percent copper, 1 percent manganese, and 0.5 percent magnesium; its mechanical resistance is much higher than that of pure aluminum.

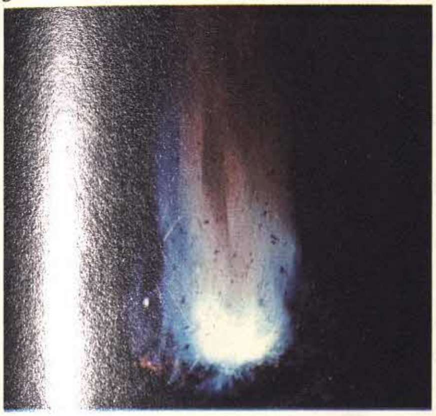
Application of aluminum for mechanical purposes requires a thorough knowledge of its properties. Special techniques are necessary to produce alloys capable of withstanding fatigue (a distortion resulting from a repeated series of stresses). Combination with other metals often causes corrosion on the contact surface because of the electrolytic characteristics of aluminum. This danger can be avoided by covering the aluminum with a layer of chromium, which adheres closely to the surface. A recently developed tech-

5a

AIRCRAFT AND MIRRORS— Illustration 5a shows a reflecting mirror, used chiefly in telescopes; Illustration 5b shows an aircraft under construction. Because aluminum is such a light metal, it is used in alloy form to build aircraft capable of speeds up to two and a half times the speed of sound. Above this speed, air friction causes overheating and aluminum structures are severely weakened.

5b

6



ALUMINUM FLASH—Once used as a combustible substance for flash photography, aluminum burns with a blue-white light of considerable brightness.

nique, used chiefly in aircraft construction, involves bonding the two metals together with epoxy resins rather than with nails.

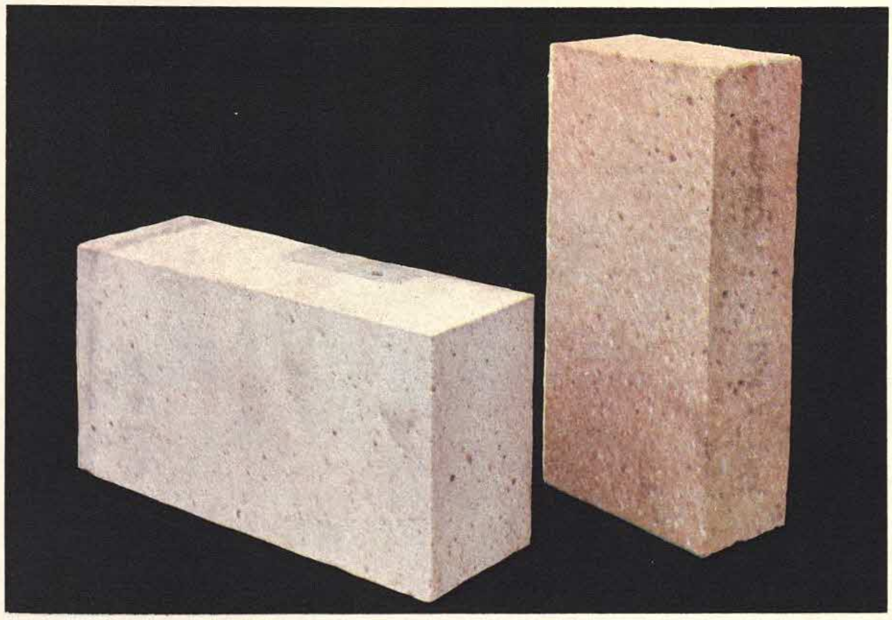
Aluminum can be used with good results in aircraft parts if the speed of the aircraft does not exceed 2.4 times the speed of sound; at greater speeds, the structure becomes overheated due to air compression and even the best alloys are weakened. This danger is avoided by using stainless steel instead of aluminum.

ALUMINUM OXIDE

Aluminum displays great affinity for oxygen and burns with great heat in air or oxygen when finely divided. When mixed with the oxides of most other metals and heated, it extracts the oxygen from them and combines with it. The process known as aluminothermy is based on this property. This process is used to produce elementary chromium and manganese. Aluminum combined with iron oxide produces a mixture used to weld iron components when other welding techniques are invalidated by the complexity (or unwieldiness) of the pieces involved. In addition to aluminum powder and powdered iron oxide, this mixture also contains silica sand. The reaction is started by burning a strip of magnesium and then proceeds spontaneously. The iron is reduced by the aluminum and fuses on the piece to be welded.

Aluminum oxide (alumina) is used chiefly in the manufacture of refractory

7a



7b

TWO SPECIAL USES OF ALUMINA—Illustration 7a shows two refractory bricks containing 95 percent alumina and resistant to high temperatures. Illustration 7b shows a sample of finely powdered alumina, used as a support in column chromatography.

(heat-resistant) bricks. When finely divided, purified, and sorted according to the size of the grains, it is used as an abrasive in optics and machining, and to make grinders or abrasive wheels. Alumina is also used as a support in column and gas chromatography. Powdered alumina acts as a dehydrator and catalyst in a number of reactions. It has a high melting point—about 2,000° C (about 3,632° F)—and is quite heat resistant. It is now possible to prepare fine synthetic monocrystals of alumina; the colored varieties are used to replace natural gems in jewelry. Extremely pure alumina also is used to make windows for optical instruments because of its special property of transparency to both ultraviolet and infrared rays.

CHEMICAL PROPERTIES

Aluminum behaves as a trivalent element in its more common compounds. Several types of oxides and hydroxides with various degrees of stability exist. Some of these are important in that they are intermediary stages in reactions used in the production of alumina and aluminum. Aluminum produces many salts, including chlorides, fluorides, sulfides, and nitrates, the most important being aluminum sulfate, $Al_2(SO_4)_3$. Combined with potassium sulfate, the double potassium aluminum sulfate $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ is produced. This salt, known generally as alum, is important in the tanning, dyeing, and paper industries. It acts as a mordant, forming insoluble colored compounds with many organic dyes.

Aluminum in the elementary state is composed of only one natural isotope of mass 27.

OXYGEN | the vital element

Oxygen is one of the elements in Group VIA of the periodic table. The others in this group are sulfur, selenium, and tellurium. These elements are characterized by having six electrons in their outermost electron shell—and a tendency to produce bivalent negative ions. Whereas the other three elements in this group can occur in valences up to +6, oxygen cannot coordinate more than two electrons.

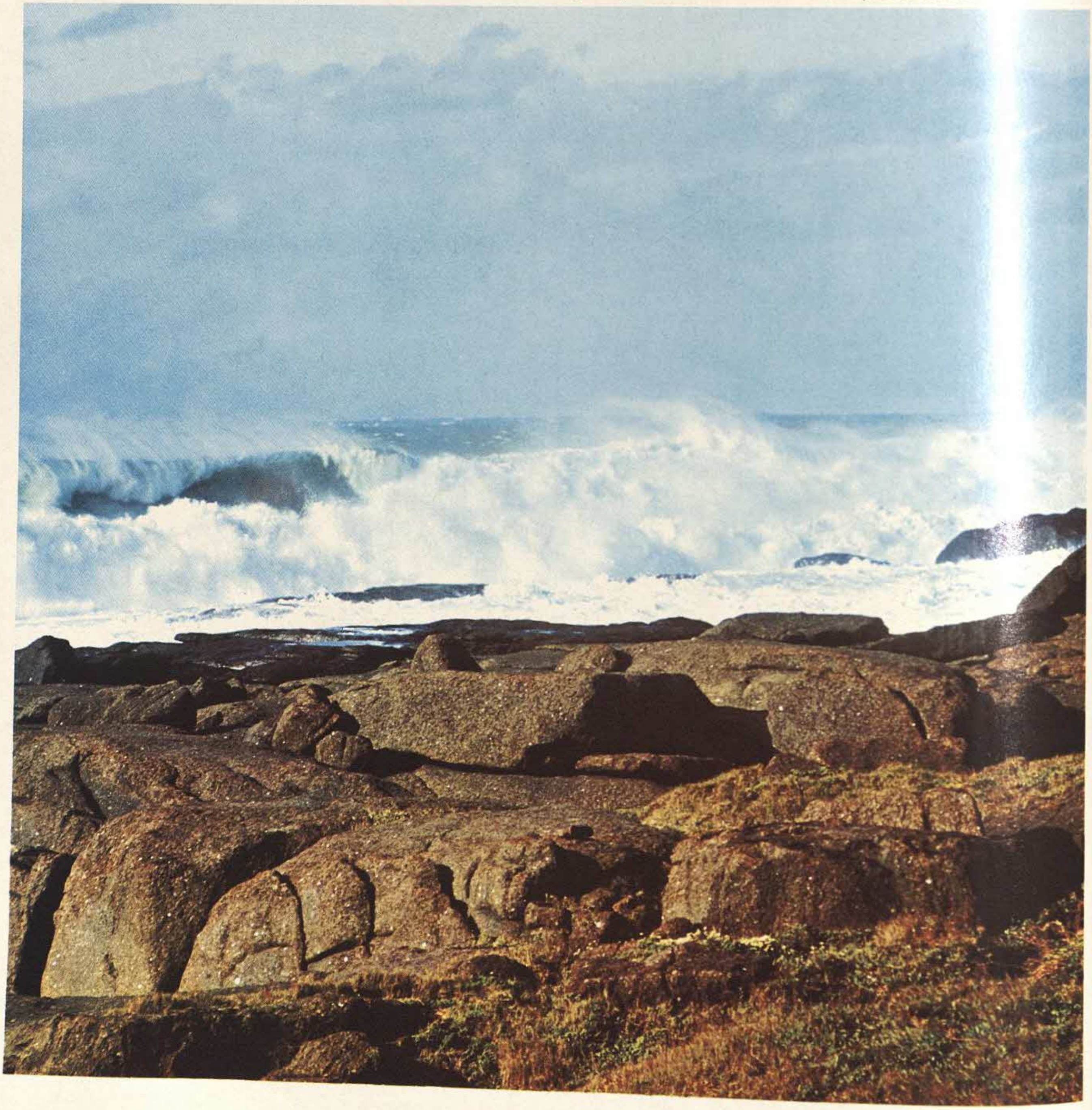
Oxygen is by far the most important of the elements in the lithosphere, accounting for about 50 percent of its weight. Oxygen makes up 21 percent of the volume of the atmosphere; eight-ninths of the mass of the oceans is oxygen.

The human body itself is two thirds oxygen and the presence of oxygen—both free and combined with other elements—is essential to life as man knows it.

A PLANET RICH IN OXYGEN

In contrast to the other planets of the solar system, the Earth is rich in oxygen. Jupiter and Neptune lack oxygen completely; they seem to be composed of hydrogen or nonoxygenated compounds and other light elements. Mercury and Mars have atmospheres almost certainly lacking oxygen, at least in its free state, although oxygen might be present in the molecules of their rocks. Only on Venus has the presence of oxygen been confirmed, in the form of carbon dioxide—the oxygen-carbon compound that is the

OCEANS, ROCKS, AND ATMOSPHERE—Oxygen is incorporated into the rocks, oceans, and atmosphere of the Earth. The greatest part is in the rocks and is combined mostly with silicon—the most ancient form of oxygen—but also with smaller quantities of other elements. Many millions of years of chemical actions have resulted in the dissolving of much oxygen into water. Further chemical actions over more millennia—including the photosynthesis process of plant life—resulted in the liberation of free oxygen into the atmosphere. The oxygen level in the atmosphere is maintained by the same process of chlorophyllic photosynthesis that helped to form it.



chief support of vegetable life on Earth.

THE OXYGEN CYCLE

The cycle that oxygen undergoes as the principal support of life is complex: plants extract oxygen by chlorophyllic photosynthesis, using the carbon dioxide of the atmosphere and combining it with water, presumably according to the following reaction:

$$CO_2 + H_2O \rightarrow H{-}C\overset{\displaystyle \nearrow O}{\underset{\displaystyle \searrow H}{}} \quad + O_2.$$

The resulting simple organic compound —formaldehyde—then goes through several complex reactions, building up to the amino acids and proteinaceous substances essential to animal matter.

The formula for the formation of formaldehyde by photosynthesis also shows the release of elementary oxygen. This is returned to the air by plants, where it is reused by plants as a constituent of carbon dioxide, or by animals through their breathing.

Breathing is a form of combustion that supplies animals with the energy they need, and returns oxygen to the air in the form of carbon dioxide—reused in turn by plants. Carbon dioxide is also given off during the decomposition of dead animals and plants, completing the oxygen cycle.

Most of the world's supply of oxygen is found in rocks, where it is primarily combined with silicon and appears to a lesser extent in combination with other elements. The free oxygen in the atmosphere is now believed to be entirely due to the process of photosynthesis.

THE DISCOVERY OF OXYGEN

The fact that oxygen exists in the atmosphere in a free form makes it plausible that its discovery would be easy. The actual history of the discovery of oxygen belies this assumption. Because oxygen is difficult to separate from air by physical means, many of the properties of air actually due to its oxygen content were attributed to air itself. Not until 1774 did the English chemist Joseph Priestley use chemical means to generate oxygen from mercury oxide, heating the oxide by focusing the rays of the sun on it through a lens. The temperature caused decomposition, and Priestley observed that a candle burned with an extremely vigorous flame in the gaseous product, and that mice lived longer in it than in an equivalent amount of air. The Swedish chemist Carl Wilhelm Scheele recognized oxygen as one of the constituents of air; the English chemist Henry Cavendish measured the oxygen content of both air and water. Finally, the French chemist Antoine Laurent Lavoisier discovered the part played by the element in breathing, oxidation processes, and chemical reactions. Because sulfur and phosphorus burn in oxygen to form substances that yield acidic solutions in water, Lavoisier named the substance oxygen, which means "acid-former."

UNIQUE PROPERTIES

Oxygen, whether in its solid, liquid, or gaseous state, is light blue in color—the color of the clear atmosphere at high altitudes. Oxygen turns into ozone when acted on by ultraviolet rays and other agents. This serves to protect life from the rays of the sun. Ultraviolet radiation would sterilize the Earth were it not for the molecules of ozone absorbing the rays whose wavelengths are below 0.30 μm (microns).

Oxygen also has magnetic properties that enable its presence to be detected by an artificially produced magnetic field.

The most important property of oxygen to men is the support it gives to combustion. All substances (except the noble gases) combine more or less readily with oxygen. Combustion is the rapid chemical combination of various substances (combustibles) with oxygen. This reaction often develops enough heat to vaporize the combustion products, thus producing flames. Combustion in air is generally much slower and less spectacular than in pure oxygen. This is because only one molecule out of five in air consists of oxygen; thus, the oxygen comes into contact with the burning substance more slowly. Also, the heat generated acts not only on the combustion products, but also on the atmospheric nitrogen, which is inert with respect to combustion and is therefore dissipated.

OXYGEN AND ITS USES

The most important source of oxygen is the atmosphere. Large quantities of oxygen are extracted from the air by fractional distillation of liquid air. Since this process is used to produce the nitrogen used in the ammonia industry, oxygen itself is actually a by-product of this process.

In the steel industry, oxygen is blown into converters to burn away the carbon in cast iron; in the nitric acid industry, oxygen is used to oxidize ammonia. Another common use of oxygen is in cutting sheet metal. The flame produced by the combustion of acetylene in oxygen is hot enough to cut metal by liquefying it. If the flame is extremely rich in oxygen, part of the molten metal is also oxidized, and the reaction is so clean that only a very small amount of acetylene is needed to maintain the flame.

Pure oxygen is used in cases where air is not available for breathing, as in spacecraft, high altitude aircraft, and submarines. Breathing pure oxygen (rather than oxygen mixed with nitrogen, as in the air) is harmless provided the pressure of the oxygen does not exceed the pressure of the atmosphere. In the case of deep sea divers and underwater swimmers using elastic diving suits, the oxygen must be diluted with inert gases, the least expensive of which is helium.

PHYSICAL PROPERTIES AND COMPOUNDS OF OXYGEN

Small quantities of oxygen for laboratory experiments can be obtained either by electrolysis or by heating potassium chlorate. Industrially, oxygen is produced by electrolysis of water, or by the fractional distillation of liquid air. Since nitrogen boils at $-195.8°$ C (about $-319°$ F) and oxygen boils at $-183°$ C (about $-297°$ F), the oxygen in liquid air is the first to distill. Oxygen has an allotropic form—ozone—that is a molecule with three oxygen atoms instead of two. Ozone oxidizes substances much more energetically than does oxygen, which is why it is used as a sterilizing agent. Ozone can be produced by controlled electric discharges in special apparatus.

The oxygen compound most important to life is water. Related to water is hydrogen peroxide (H_2O_2) obtained by electrolyzing sulfuric acid under special conditions. Diluted with water, hydrogen peroxide is used as a mild disinfectant. It is also used in cosmetics as a bleaching agent. When mixed with potassium permanganate, it produces a strong exothermic reaction, with the development of water vapor and a sharp increase in volume. This property is used in the aerospace industry, where oxygen is used to produce the vapor required to activate turbopumps that feed liquid-fuel rocket engines.

Oxygen is basically a bivalent element. Another of its chemical properties is that of forming anhydrides with metalloids. This is why Lavoisier called oxygen the "acid-former." It is now known that the combination of oxygen with most other elements produces the oxides, many of which then react with water to produce acids or hydrates, depending on the character of the element.

CALCIUM | skeletons, concrete, and soap scum

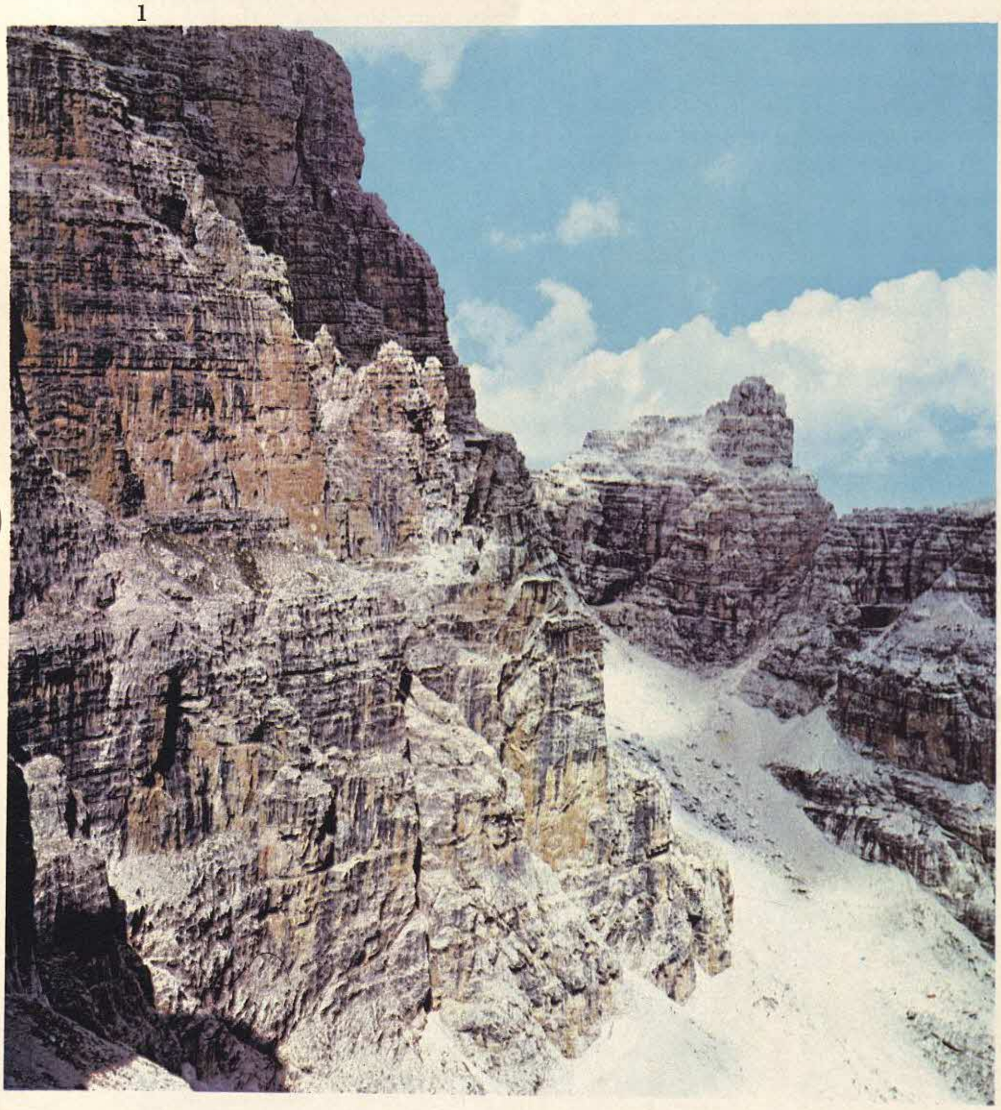
Not only is calcium (Ca) the fifth most abundant element in the Earth's crust, forming about three percent of its substance, but it is one of the most essential ingredients in the bones and teeth of vertebrates, the shells of mollusks, and plant leaves.

Aside from its role in biology, calcium forms the most economic base in the chemical industry, providing a compound with countless applications. In addition, the limes and cements used in building are largely made up of calcium compounds. The multiple uses of this element also include the reduction of uranium for use as a nuclear fuel.

DISCOVERY AND ISOLATION OF THE PURE METAL

Both calcium oxide (quicklime) and cal-

1



THE DOLOMITES—Calcium is found in many rocks, including the Dolomite Mountains in northern Italy. These formations are composed entirely of calcium and magnesium carbonate, $CaCO_3 \cdot MgCO_3$. The Dolomites were formed during ancient geological periods by the accumulation of seashells.

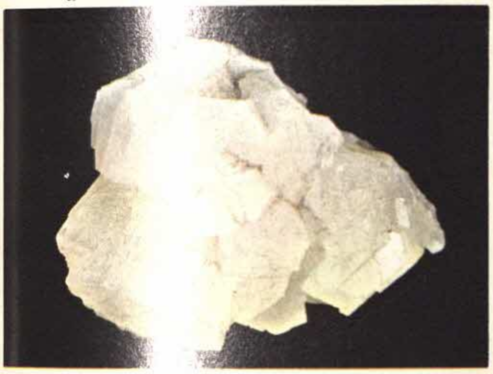
MARBLE, A PURE CALCIUM CARBONATE—Marble as used in the arts and architecture, especially when containing colored veins, is composed of almost pure calcium carbonate. The variegations are made up of trace impurities. Generally, the carbonate in many calcareous rocks is pure enough to prepare the oxides and hydroxides for cement.

2

3

CRYSTALLINE CALCIUM CARBONATE—In its pure state, calcium carbonate crystallizes in two modifications, aragonite (Illustration 3a) and calcite (Illustration 3b). Calcite crystals are transparent to a broad light spectrum, from infrared through the visible range, and into the ultraviolet frequencies. Illustration 3c is a sample of Iceland spar, an extremely clear calcite with the property of birefringence or double refraction. Light passing through such a crystal is split, creating a double image.

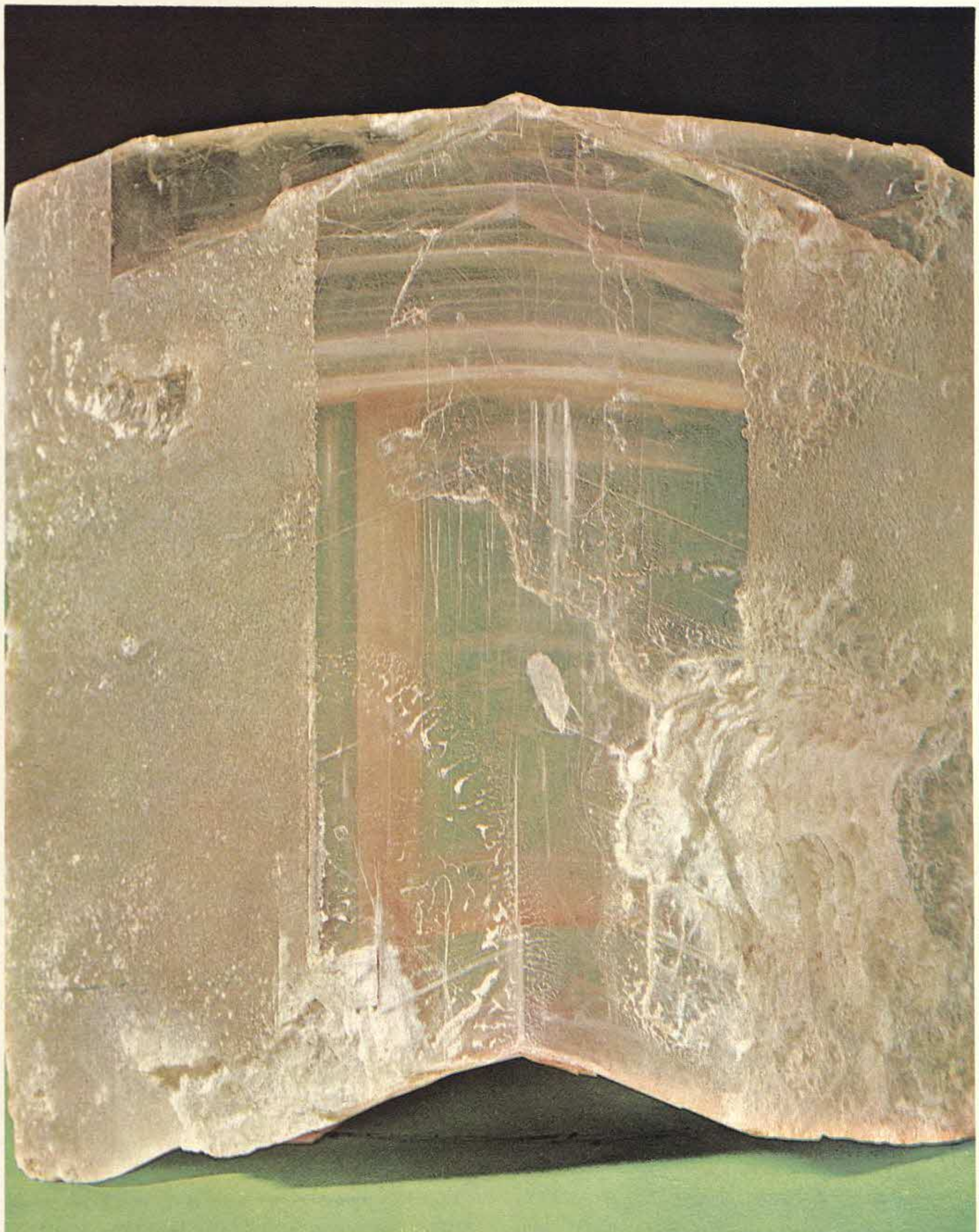
a



b

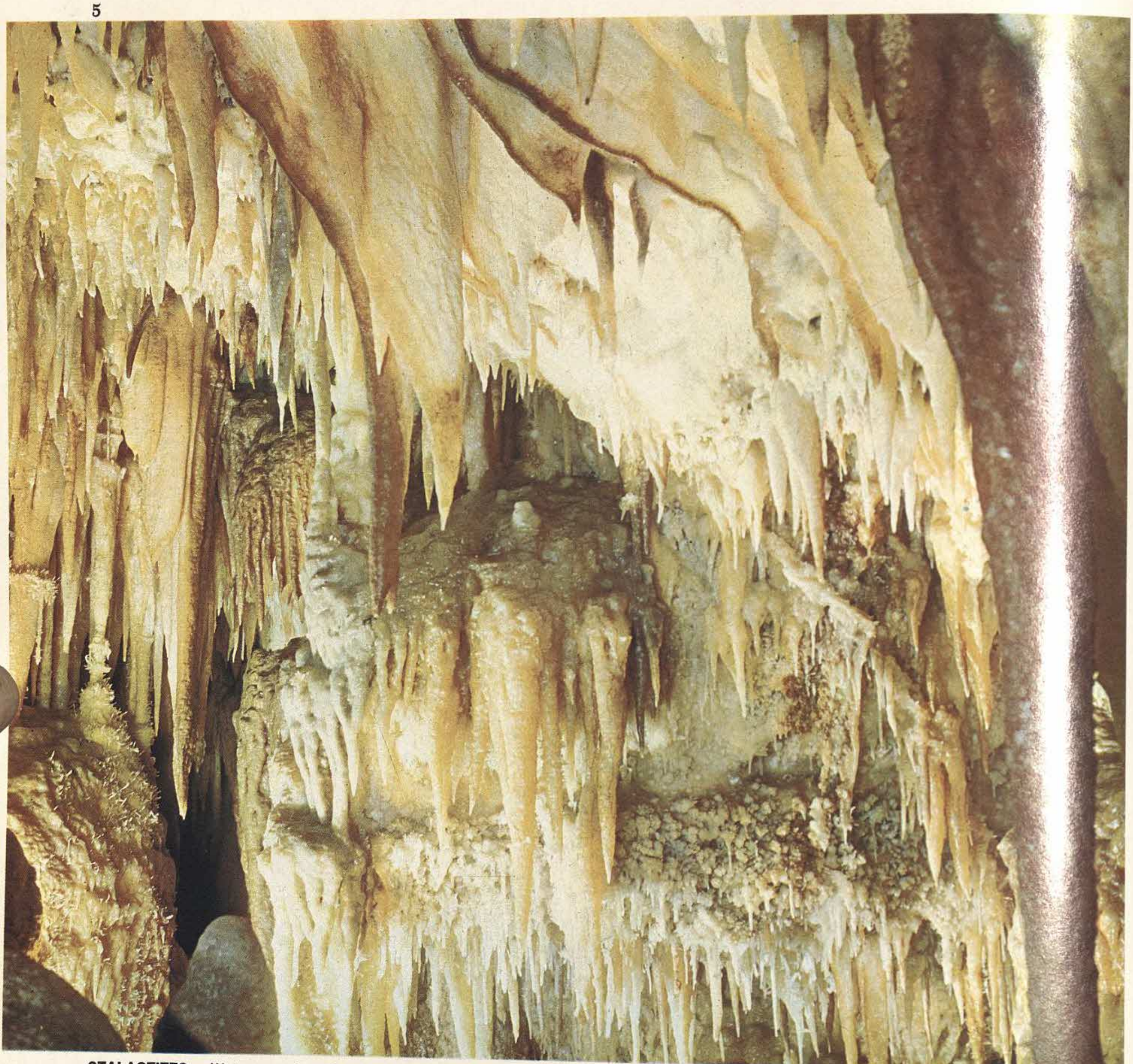
c

4



CALCIUM SULFATE (GYPSUM)—This excellent specimen of a gypsum crystal is composed of calcium sulfate, $CaSO_4 \cdot 2H_2O$. Although this sample was deposited and redeposited by underground water, gypsum is also obtained from deposits crystallized from seawater, which always contains calcium sulfate. When heated, some of the water is driven off, forming a semihydrate. Easily rehydrated, its use in construction is based on this process. Gypsum has been used in building construction since ancient times.

5



STALACTITES — Water passing through the subsoil is rich in carbon dioxide and, therefore, somewhat acid. This allows it to dissolve appreciable quantities of calcium carbonate from rock. In the process, caves are formed. The hanging stalactites and rising stalagmites in caverns and caves are formed when the water evaporates, leaving behind limestone. The centuries of dripping water have created the fragile-looking but solid "icicles" of calcium carbonate shown here.

cium hydroxide (slaked lime) were known and used by the Romans in the first century. In fact, the Latin word *calx* (lime) provides the basis for the name of the element. Not until 1808, however, was elementary calcium successfully prepared. Initial research was first carried out by the Swedish chemist J. J. Berzelius and a colleague; the two prepared a calcium amalgam. Later, the English chemist Sir Humphry Davy independently isolated an impure sample of the metal from a similar amalgam.

Physically, calcium is a relatively hard, silvery-white metal. Chemically, it is a member of the Group IIA alkaline earth elements, with a valence of +2. Exposed to the atmosphere, it rapidly becomes coated with a white layer of calcium nitride by reacting with nitrogen. Metallic calcium burns with a typically yellow-

red flame, though traces of sodium, strontium, or barium will mask this color. Thus, flame tests for its presence cannot be conclusive without careful measurement of the wavelength of the emitted light.

Pure calcium is an excellent reducing agent, and is used as such in the metallurgical treatment of other metals to prevent surface oxidation. Because of a strong affinity for oxygen, it can extract this element from many oxides, binding it to itself. This affinity is the basis for the technique called calciothermy.

QUICKLIME, SLAKED LIME, AND CEMENT

Quicklime is the common name for calcium oxide, CaO, a compound easily obtained by heating the carbonate, $CaCO_3$. This procedure consists of mixing the crushed carbonate with carbon; the mixture is then fed into the top of a cylindrical oven. The carbon burns in an upward current of hot air, the resultant heat producing the reaction: $CaCO_3 \rightarrow CaO + CO_2 - 42.5$ calories. The quicklime is a transparent mass that rapidly becomes covered with a fine layer of calcium hydroxide on exposure to atmospheric moisture. Melting only at temperatures above 2,500° C (4,532° F), calcium oxide is often used as a refractory lining in high-temperature furnaces.

Calcium hydroxide, $Ca(OH)_2$, or slaked lime, is formed by the addition of water to the oxide, either naturally through water taken from the atmosphere or by mechanical addition. The solution formed is decidedly alkaline, although calcium hydroxide is only moderately soluble in water. As a construction material, it has innumerable uses. In chemical analysis, a solution of calcium hydroxide is used to detect the presence of carbon dioxide, with which it forms a white precipitate of calcium carbonate.

This reaction with carbon dioxide and the conversion to insoluble calcium carbonate is the basis for the "setting" reaction of cement and concrete: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$. Since this reaction depends on the contact of the cement with atmospheric carbon dioxide, the setting usually lasts for some time, perhaps years. As the reaction progresses, the water formed can be seen as moisture on the surface of a cement structure.

Modern construction techniques have overcome the prolonged setting time, however, not only in the manufacturing of so-called quick-setting cement, but in the making of precast concrete components. Initially, the concrete is prepared in a normal manner and formed into the desired shapes. These are then heated under pressure, with air replaced by carbon dioxide. This is dissolved in the concrete's water while being forced throughout the concrete object, causing it to set rapidly.

IMPORTANT COMPOUNDS

In addition to the oxide and hydroxide, another important calcium compound is the chloride, $CaCl_2$. This is an extremely hygroscopic salt, absorbing great quantities of atmospheric moisture. In fact, exposed to the air, the salt readily goes into solution with the water it extracts.

In aqueous solution, calcium chloride forms hydrates containing a considerable number of water molecules. This can effectively lower the freezing point of water as much as 50° C (90° F). In cold climates, calcium chloride is commonly used on icy pavement to melt ice, although the actual mechanism is the lowering of water's freezing point. Another common application uses the compound to keep the dust down on unpaved roads. In this instance the chloride's hygroscopic property keeps the roads damp.

Calcium carbide, CaC_2, was once used as a fuel for acetylene lamps in which acetylene gas was produced by adding water to the compound. Although such illumination has long been replaced by electricity, calcium carbide remains important because acetylene is now used as a raw material to make calcium cyanamide, $CaCN_2$, a valuable synthetic nitrate fertilizer. This material is an excellent source of agricultural ammonia because it releases the ammonia quite slowly in the presence of water. Acetylene is a dangerously explosive gas, unstable at low pressure.

CALCIUM AND WATER HARDNESS

Water hardness is a way of expressing the concentration of calcium ions dissolved in the water. Actually, only two calcium salts are responsible for hardness in water: calcium sulfate and calcium bicarbonate. (It should be noted that there are two types of hardness, temporary and permanent. Temporary water hardness can be overcome by simple boiling, while permanent hardness cannot. The sulfate and bicarbonate account for the latter type.)

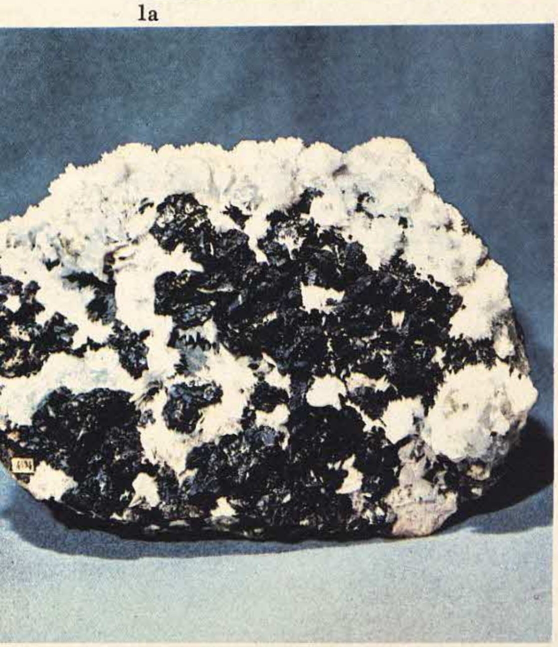
For a number of reasons, it is highly desirable to remove any calcium salts from water. This is especially true in steam boilers where permanent hardness results in a buildup of scale. Almost like a wall of stone, scale composed of calcium sulfate and bicarbonate can reduce the efficiency of a boiler considerably, and can actually block hot water pipes. In another instance, calcium ions severely hamper the cleansing ability of soap. Common soap scum, or "bathtub ring," is actually an insoluble precipitate of a calcium soap. Suds will not form in hard water until all the calcium has been precipitated, and suds are a common measure of soap's cleaning ability.

Modern technology can eliminate water hardness by such methods as devices containing ion-exchange resins. Hard water passing through these resins has its calcium ions replaced by other ions that do not create hard water. Today's synthetic detergents also soften water by incorporating phosphate compounds that react with calcium ions to pull them out of the solution. However, phosphates have been found to pose serious pollution problems—they create rapid growth in marine plants—and research is testing substitutes.

The natural process by which all bodies of water age because of the accumulation of nutrients is known as eutrophication. This phenomenon can be greatly accelerated when excessive nutrients, such as those in detergents, accumulate in the water. Detergents are rich in phosphates and nitrates that fertilize prodigious blooms of algae, the simplest aquatic plants. As the algae decompose, the dissolved oxygen in the water is used up, the water looks and tastes bad, the fish die, and so does the water slowly die because of accelerated eutrophication. In an effort to keep it at a minimum, scientists are examining detergents for biodegradability and toxicity to fish.

ZINC | garbage cans and hydrogen generators

1a



1b

BLENDE AND CALAMINE — Zinc sulfide, or blende (Illustration 1a), forms characteristic crystals giving the overall impression of delicate white flowers. Zinc silicate, $Zn_2SiO_4 \cdot H_2O$ (Illustration 1b), called calamine or natural hemimorphite, forms ricelike transparent crystals.

Before it was recognized as a distinct element, zinc (Zn) was used for making brass and is referred to in the Old Testament. Older still are samples of an alloy containing high percentages of the metal; these relics were found in prehistoric ruins in Transylvania. Zinc, itself, appears to have been prepared in thirteenth-century India by the reduction of one of its silicates with organic matter. The metal was rediscovered in 1746 by a European chemist who showed that zinc could be obtained by reducing calamine (the same silicate used in India five centuries earlier) with charcoal.

NATURAL ABUNDANCE

Zinc is a relatively common element, and because its minerals tend to be concentrated in rich deposits it is quite easily extracted. In this respect, zinc can be contrasted to those elements that are more abundant than zinc but are more widely distributed, making extraction a more costly operation.

The principal zinc ores include sphalerite, or blende. This, the natural sulfide of zinc with the formula ZnS, often occurs in association with lead sulfide (galena), and sometimes with pyrites, or iron sulfide. Smithsonite, natural zinc carbonate, and calamine, a silicate, are other important minerals. A fourth principal ore is the complex mineral franklinite, composed of zinc, manganese, and iron oxide.

Zinc deposits are not only important commercially for the zinc they contain, but also because of their association with other valuable elements. When the zinc deposits were formed, minerals containing lead, cadmium, and germanium often formed concurrently. Zinc minerals, in fact, are an important source of cadmium.

EXTRACTION OF ZINC

Two methods are commonly employed to extract zinc from its ores: roasting and electrolysis. In the roasting operation, the ores are heated to form zinc oxide. A second step reduces this oxide to the metal with coal or carbon, and the molten mass is distilled to produce a purified material. Although less used, electrolysis is commercially important because it al-

SMITHSONITE—This is natural zinc carbonate, $ZnCO_3$, another of the common ores of zinc.

2

3a

3b

FRANKLINITE AND HYDROZINCITE—Illustration 3a is a specimen of a zinc oxide-iron oxide mineral called franklinite. Traces of manganese often occur in this mineral. The characteristic fingerprint pattern identifies the basic zinc carbonate hydrozincite shown in Illustration 3b.

lows recovery of zinc from relatively low-grade ores. In this process the ores are crushed and dissolved in sulfuric acid. Electrolysis of this solution results in zinc with a high degree of purity.

THE USES OF ZINC

Zinc is primarily used as a metal, although its compounds have many important applications. About one third of the present zinc production goes into the galvanizing of ferrous metals, notably iron. To protect such metals from corrosion, a thin layer of zinc is deposited by immersion in molten zinc. While a fine coating of basic zinc carbonate forms on the surface of the treated metal, the underlying iron is completely isolated from atmospheric attack. The zinc oxide forms a protective barrier for the zinc, preventing further oxidation.

Brass alloys consume another third of the world zinc production, while the remaining zinc is converted into a number of chemical products. In the making of alloys, the greater the percentage of zinc the less costly the finished product, for copper (which is used in bronze) has increased tremendously in price. Although brass is being displaced to some extent by aluminum alloys in a number of fields, brass continues to rank as one of the most important commercial alloys.

The largest single use of zinc in the United States is for die-casting alloy. In the die-casting process, molten metal is injected under pressure into a steel die. The metal solidifies in this die almost at once, and the die can be opened and the casting ejected rapidly. The process lends itself to the fast production of complicated parts because the whole sequence can be operated automatically. Zinc forms

the basis for one of the best alloys for die casting when alloyed with 4 percent aluminum and 0.05 percent magnesium. It is essential in the formulation of this alloy that only the highest purity zinc be used, and care is taken to prevent contamination by low-melting-point metals such as lead, cadmium, or tin; otherwise the castings are subject to intercrystalline corrosion.

Such an alloy melts with great ease, is fluid, and does not attack the steel dies into which it is injected. It can reproduce precisely the shape of the most complicated dies. The cast parts, which have good mechanical properties, can be plated or lacquered easily. For these reasons, the automobile industry uses large quantities of zinc die castings, for radiator grills, carburetors, fuel pump and shock absorber bodies, door handles, instrument panels, and other applications. Zinc die castings are used extensively also in electrical appliances, machine tools, building hardware, and toys.

In building construction, zinc rolled into a sheet gives long service. A development in rolled zinc involves the introduction of an alloy containing small quantities of copper and titanium, which impart improved stiffness and creep resistance. An important use of rolled zinc is in the production of dry battery cans, which form the container and one electrode of the Leclanche type of cell, the unit on which most portable dry batteries are based.

Zinc dust, made either by rapid chilling of zinc vapor or by atomizing molten zinc, is used in the manufacture of dyestuffs and other chemicals. It is also used in the manufacture of sodium hydrosulfite, a reducing agent. Zinc dust is used in precipitating gold from cyanide solutions. In sprayed form, the dust is used in paints.

THE PROPERTIES OF ZINC

Zinc, with atomic number 30, is a Group IIB element, sharing its family with cadmium and mercury. The metal has a blue-white luster, and is brittle at room temperature. Heated to between 100° C and 150° C (212° F and 302° F), however, zinc becomes quite malleable; it reverts to a brittle state at higher temperatures due to changes in crystalline structure. Zinc melts at a relatively low 419.4° C (about 786° F), which is just slightly above the melting points of tin and lead.

Zinc easily replaces hydrogen in acids, a property commonly used in the commercial production of the gas. The metal is typically electropositive, and has an oxidation state of +2. In the liberation of hydrogen from acids, zinc reacts with both oxidizing and reducing compounds (sulfuric acid, H_2SO_4, and hydrochloric acid, HCl, for example).

Exposed to atmospheric oxygen, zinc readily forms a white oxide. If heated to red heat, the metal burns to form the same compound. Because zinc easily forms compounds with oxygen, it is widely used in organic reactions to remove oxygen from organic molecules.

Although zinc and its salts are mildly toxic, recent research indicates that traces of the element are essential to plant and animal life.

ZINC COMPOUNDS

One of the simplest zinc compounds is the oxide, ZnO, occurring naturally as the mineral zincite. Synthetically, the compound is prepared by burning the metal in air. Primarily, zinc oxide is used as a pigment and in the rubber industry. As a pigment, its covering power, or opacity, is second only to that of titanium dioxide.

Certain therapeutic properties allow the use of zinc oxide in astringent and disinfectant preparations. Zinc also forms a peroxide, $ZnO_2 \cdot \frac{1}{2}H_2O$, that, like hydrogen peroxide, is capable of releasing oxygen. This compound is sometimes used as an antiseptic.

Zinc hydroxide, $Zn(OH)_2$, has an obviously alkaline character. However, in the presence of stronger bases it may behave as a weak acid. This amphoteric property allows it to form compounds known as zincates in an environment rich in hydroxyl ions.

Of the many zinc salts, the more important are zinc chloride, zinc sulfate, and zinc sulfide. Zinc chloride is the product of a reaction between the metal and hydrochloric acid. On evaporation of the solution, zinc chloride forms crystals containing three or six water molecules. In the anhydrous state, this compound is a powerful dehydrating agent and is used in organic reactions to eliminate water.

Molten zinc chloride has the property of being able to clean metallic surfaces, which enables them to be welded efficiently. This property makes zinc chloride valuable as a flux in industrial welding operations. Similarly, a concentrated solution of zinc chloride and zinc oxide forms the oxychloride, $Zn(OH)Cl$, which is an effective adhesive for joining dissimilar materials. In aqueous solution, the chloride finds some use as a disinfectant.

Zinc sulfate, $ZnSO_4$, is used in electroplating, textile printing, and coagulating viscose rayon. By mixing zinc sulfate with barium sulfide, a double exchange reaction occurs to produce the highly opaque white pigment called lithopone. Because it is less costly than the zinc oxide pigments, lithopone is often used in their place.

Zinc sulfide, ZnS, occurs naturally as blende, one of the most common zinc ores. Synthetically, the sulfide can be prepared by precipitation in the reaction between ammonium salts and hydrogen sulfide, producing a white compound. If the sulfide contains traces of heavy metal salts as impurities, it phosphoresces.

COPPER | the tawny king of electrical and heat conduction

1a

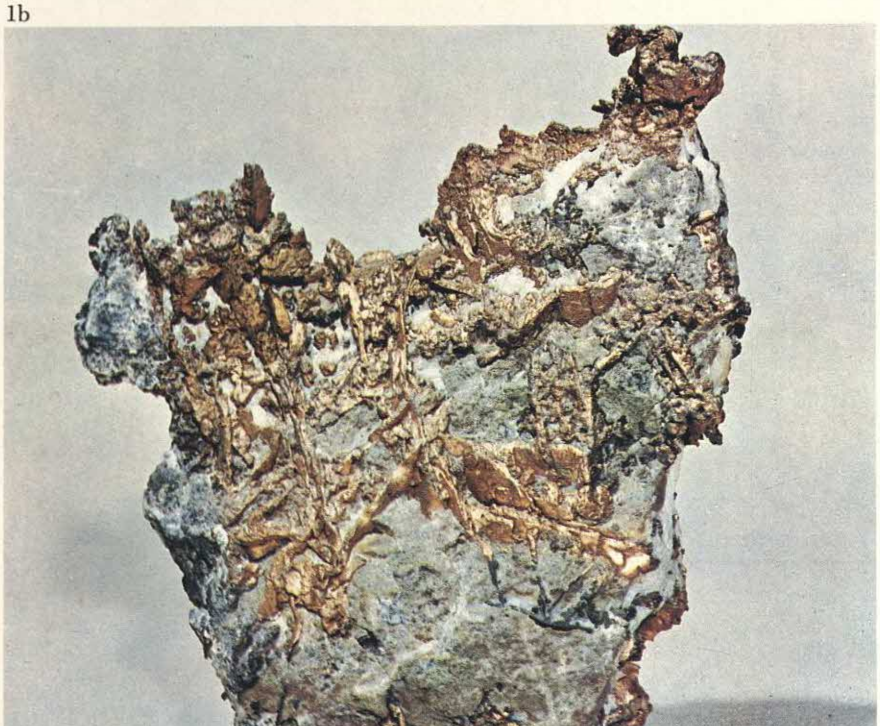
2

History gives a special place to the primitive man who first learned how to extract copper from the earth and convert it to his use as a workable metal. His discovery, perhaps around 4000 B.C., prepared the way for a still more important find: a means of fusing copper with tin to form bronze. Bronze made obsolete the weapons and tools of stone and bone, enabling man to step from the Stone Age into the age of metals. Important as copper was to ancient man, it is perhaps more important to modern man as a conductor of electricity, as the principal component of many alloys, and as a constituent of many substances used in laboratory analysis or industrial processes.

COPPER IN NATURE

Copper is one of the most common metals, contained in the crust of the Earth in a proportion of 70 g/t (about 2.5 oz/t). There are large deposits of copper in the United States, Chile, the Soviet Union, Zambia, and the Republic of the Congo. Copper is often found concentrated in seams, forming extensive deposits from which extraction is relatively easy and economical. In its native state, copper is found as filaments covered by a layer that has been altered chemically; in this form, only small amounts of copper are recoverable.

1b



COPPER IN NATURE—One of the largest deposits of copper is in the United States. Illustration 1a shows an opencut copper mine in Utah, and 1b shows copper in its natural state.

CHALCOPYRITE—This sulfide ore (Illustration 2) of copper and iron, $CuFeS_2$, is widespread. One of its characteristics is the metallic reflections from its surface.

3a

3b

COVELLITE AND MALACHITE—Covellite (Illustration 3a) forms beautiful hexagonal laminae. Malachite (shown in 3b), a basic carbonate, forms knobbed crystals of an emerald green color that makes it desirable for ornamental purposes.

It is more frequently found in its oxidized state.

The most important minerals in the copper family are the sulfide ores: chalcocite, Cu_2S, and chalcopyrite, $CuFeS_2$. In many of the pyrites from which iron is extracted, there is a large copper content that can be recovered with advantage. Copper is often found with precious metals, such as silver, gold, and platinum; these can be recovered during the refining of crude copper.

Beautiful minerals from the copper family include malachite and azurite, found in the form of knobbed concretions of hydrothermal origin that show striking designs when cut into laminae, and dioptase. Malachite is much sought as an ornamental stone because it is becoming increasingly rare and valuable. Malachite is a basic copper carbonate, $CuCO_3 \cdot CU(OH)_2$, as is azurite, $2CuCO_3 \cdot Cu(OH)_2$. Dioptase is a copper silicate that is used for ornamental purposes because of its emerald green color.

EXTRACTION AND REFINING OF COPPER

Copper is usually extracted and refined by a three-stage process. In the first stage, ore is ground and enriched. In the second stage, ore is roasted in a warm current of air to remove the sulfur in the raw material. In the third stage, the crude metal is refined by electrolysis.

The grinding and enrichment process recovers copper from poor ore, even that containing only 1 percent copper. The ore is ground to a fine dust and passed through liquids containing small quantities of foam agents (oils). The grinding process separates granules of copper ore from other minerals, even if only partially. The copper ore granules are attracted into the air bubbles created by the foam agents and thus separated finally from the other mineral dust. By eliminating slag, this flotation process concentrates the copper ore that was present in the original raw material. The product that is passed on to the second stage, an iron and copper sulfide, usually contains up to 20 percent copper.

The second stage of extraction involves

4a

AZURITE AND TURQUOISE—Azurite (Illustration 4a) is a basic copper carbonate, $2CuCO_3 \cdot Cu(OH)_2$, blue in color. Turquoise, shown in Illustration 4b, which varies in color from pale blue to apple green, is sometimes called Persian turquoise because it is found widely in Iran (formerly Persia).

4b

heating the iron and copper sulfide in furnaces similar to the converters used to make steel from pig iron. Air is pumped down from above as the mineral mass is heated to a temperature of 1200° C (2192° F) to ensure that the mineral becomes fully molten. The amount of sulfur in the mineral is greatly reduced because part of the sulfur burns off during the heating process. The copper becomes oxidized first; while the iron also oxidizes, the copper is reduced partially to metallic copper. Further heating completes the reduction.

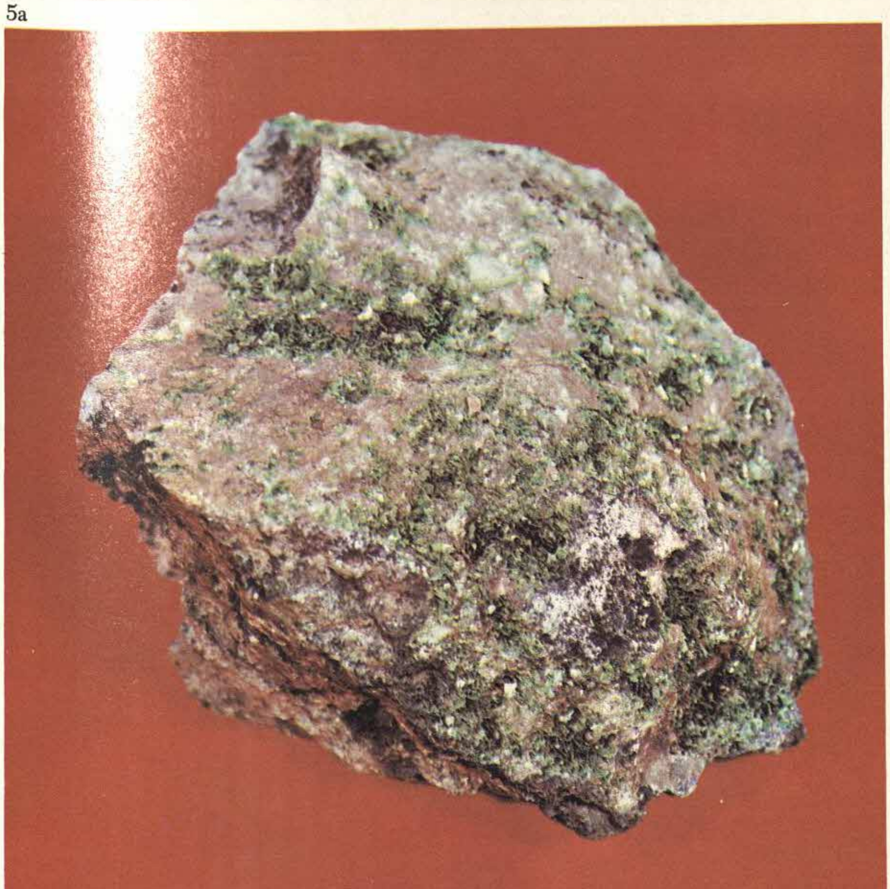
In wet extraction, a less common process, the metal is extracted in a solution. The copper ore is pulverized and left to oxidize for a time in the presence of atmospheric agents. This is essentially the process involved when minerals on the surface of rocks are exposed to the air. The ground and oxidized mineral is then dissolved in sulfuric acid and caused to precipitate while the iron is retained in solution.

Electrolytic refining involves the use of cells in which copper is introduced in the form of copper sulfate, $CuSO_4$, in a proportion of 15 percent, and sulfuric acid in a proportion of 5 to 10 percent. If a low-voltage electrical current is passed through the cell, copper with a purity of 98 to 99 percent is deposited on a cathode. A second refining process will produce copper with a purity of 99.995 percent. During the first refining, impurities collect at the bottom of the cell in the form of sludge, which often contains recoverable precious metals such as silver, gold, and platinum.

PROPERTIES AND ALLOYS

Copper is a soft, ductile, malleable metal. It is quite heavy, with a specific gravity higher than that of iron. Copper, which melts into a viscous liquid at a temperature of almost 1100° C (2012° F), is not used for casting because it does not flow freely through molds. Because the mobility of its electrons within its crystal lattice makes it a very good conductor of heat and electricity, it is used extensively in electrical wiring. Copper evaporates easily in a vacuum, making it useful in

5a



5b

TORBERNITE — The mineral torbernite, $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$ (Illustration 5a), has little practical importance. Copper is widely used in industry as an electrical conductor, much of it in wire as on the reel shown in Illustration 5b.

6

COPPER ALLOYS—Copper is used with other elements to make alloys such as bronze, from which this bell was cast, and brass. The cost of bronze, used also to make coins and statues, is high because of the amount of tin used in the alloy.

the preparation of mirrors that reflect infrared rays. It has a distinctive reddish color because it reflects radiation with a long, rather than a short, wavelength. The reflective power of copper is so high in the infrared range that a copper-covered mirror can reflect a ray from this wavelength many times without significant energy loss.

Copper forms solid solutions with gold in all proportions, and it is used with gold to form alloys with greater durability than that of gold alone. With a small proportion of copper, these alloys take on a pink color.

Copper has important applications in two important families of alloys: the bronzes, in which the second component is tin, and the brasses, in which the second component is zinc. The bronzes are hard, fragile, easily meltable, and have many mechanical uses. Because they have a low coefficient of friction when moved across steel, they are especially suitable for the bearings on which steel shafts turn. The friction coefficient is often reduced even more by the introduction of other elements. Small amounts of phosphorus or silicon are sometimes added—the phosphorus to increase durability and resistance to corrosion and the silicon to increase resistance to traction without decreasing electrical conductivity. This alloy is used for small-gauge conductors such as telephone wires when good mechanical resistance is needed in addition to good conductivity. In the brasses, the zinc content varies from 20 to 50 percent. High zinc content gives brass a light color and makes it very brittle. The addition of other ingredients gives the brasses particular resistance to corrosion.

COPPER COMPOUNDS

Copper has a valence of +1 or +2 and therefore forms two series of compounds, the cuprous and the cupric. When exposed to air, copper forms a green patina of basic carbonate. This covering protects the metal from any further atmospheric corrosion and makes it useful as a covering for roofs and the domes of churches in thicknesses of about 1 mm (about .04 in.). Although copper is corroded by nitric acid, hydrochloric acid does not corrode it, and sulfuric acid corrodes it only when the acid is hot.

Traces of copper are essential to living things, especially plants. Its soluble compounds are poisonous.

Of the cupric compounds, one of the most common is cupric sulfate, $CuSO_4$, also called blue vitriol, which has a beautiful blue color and crystallizes as a hydrate containing five molecules of water. Mixed with lime milk to form a bluish paste that kills fungi, it is used in agricultural sprays for plants (called Bordeaux mixture). Another important cupric compound is cuprammonic hydroxide, $Cu(NH_3)_4(OH)_2$, which dissolves cellulose, an otherwise indissoluble substance, without causing too many alterations in its complex molecular structure. For this reason, cuprammonic hydroxide has important applications in industry and the laboratory, where it is used to determine the cellulose content of substances such as wood and paper. Industrially, it is used to dissolve cellulose so that it can be extruded from baths of the resulting solution in the form of very fine threads. These threads harden quickly in the air and become rayon, a fiber for textiles.

Of the cuprous compounds, cuprous oxide (Cu_2O), a red crystalline material, can be produced by electrolysis or furnace methods. It imparts a red color to glass and is used in paints. Cuprous chloride ($CuCl$) is prepared by treating metallic copper and cuprous oxide with hydrochloric acid and is used in gas analysis. Cuprous sulfide (Cu_2S) occurs in nature as the mineral chalcocite.

COPPER SULFATE—Crystals of copper sulfate, also called blue vitriol, are a beautiful, intense blue. Mixed with lime milk, copper sulfate is called Bordeaux mixture and is used as a fungicide.

7

FLUORINE AND CHLORINE | chemistry's terrible twins

Although the action of fluorine (F) on other substances was noted in the sixteenth century, not until 1886 was this most reactive of all elements isolated. For over three hundred years, chemists of various capabilities had tried unsuccessfully, and often with tragic results, to tame this gas that fiercely attacks anything it contacts. Both the Swedish chemist Carl Scheele and the English chemist Sir Humphry Davy, among other great names in chemistry, experimented with hydrofluoric acid. However, the honors—culminating in the Nobel Prize for chemistry (1906)—fell to the French chemist Ferdinand Moissan for isolation of elemental fluorine in the last quarter of the nineteenth century. To this day, variations of Moissan's methods are responsible for the commercial production of fluorine, atomic number 9.

With a less protracted history, chlorine (Cl) was discovered in 1774 by Carl Scheele. He did not recognize his discovery as a distinct element, however, and it was left to Sir Humphry Davy to isolate and name the element in 1810.

Chlorine, with atomic number 17, is less reactive than its fluorine "twin," although it, too, is a vigorously active gas.

PHYSICAL AND CHEMICAL PROPERTIES

Both fluorine and chlorine are members of the halogen family, and both are gases in their normally observed states. Gaseous fluorine is pale yellow in color, with a characteristic pungent odor that indicates its presence in concentrations as small as 20 parts per billion of air. Fluorine is the most reactive of all the elements; virtually no inorganic or organic substance is immune to its attack. Because of this extreme combining power, elemental fluorine is never found in the free state in nature, although it is widely distributed chiefly as the minerals fluorspar, CaF_2, and cryolite, Na_3AlF_6. Other minerals complete its pattern of distribution to place fluorine in the thirteenth position on a scale of abundance in the Earth's crust.

Chemically, the valence of fluorine is always −1, due to the fact that its diatomic molecule readily gains an electron. In this respect, fluorine is always found as the F_2 molecule, in which one electron is shared by two atoms. Thus, the fluorine molecule can be pictured as $:F:F:$ in which each atom contributes an electron to the circled pair.

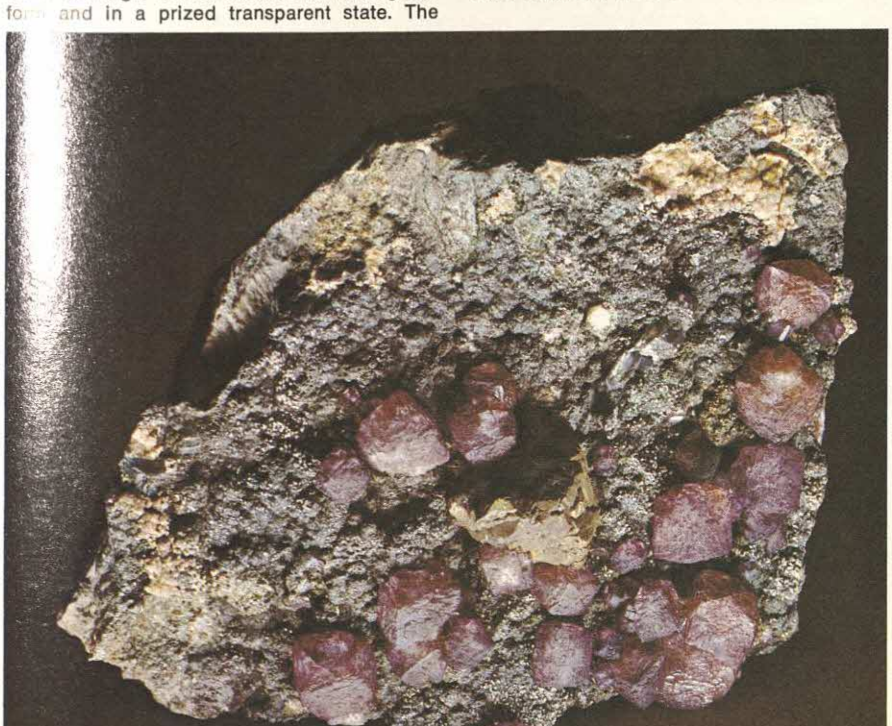
All metals react with fluorine under suitable conditions, notably at elevated temperatures. In many cases, the fluorine forms a protective fluoride coating on the surface of the metal, preventing further reaction. However, since such fluorides are generally quite volatile, continued exposure to high temperatures does not prevent on-going reactions. In the case of

1

SALINE — Man's largest chlorine reserve is found in the seas, with a estimated average abundance of 0.2 percent. Sodium chloride, representing most of this content, can be recovered by concentrating seawater and evaporating the solution, as seen in this illustration.

FLUORITE—Fluorine's name is derived from this mineral, which is the element's most characteristic and important source. The specimen shown here illustrates violet crystal formations, although fluorite also occurs in a green form and in a prized transparent state. The latter has been used to make delicate and precise objective lenses for microscopes because of its extremely low index of refraction. Its fragility, however, has led to the use of other materials, most of them man-made.

2



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CRYOLITE—Another fluorine mineral, with the formula Na_3AlF_6, is represented by this sample of cryolite. Found primarily in the United States, Greenland, and the Soviet Union, cryolite sometimes has a pinkish hue.

4a

4b

SYLVITE AND CARNALLITE—Both these minerals contain chlorine. Sylvite (Illustration 4a) is a simple compound of potassium chloride, while carnallite (Illustration 4b) is a more complex double salt of potassium and magnesium chlorides. The salmon pink color of the latter is due to iron impurities. Normally, both occur as translucent masses. Sylvite crystals are usually colorless, but sometimes they are a bright, translucent blue.

the more reactive alkali and alkaline-earth metals (sodium, potassium, and magnesium, for example), no resistance is offered by such surface fluorides, and the reactions with these elements are highly exothermic. Less reactive metals and most nonmetals, especially when in a finely divided state, and even water, burst into flame in a fluorine atmosphere. Certain metals form fluoride coatings with relatively low levels of volatility. Among these are aluminum, copper, and nickel; these are used to make containers for storing the gas.

Among the organic compounds, only carbon tetrafluoride does not enter into immediate reaction with elemental fluorine. In fact, the reactions between fluorine and organic materials tend to be quite violent and dangerous unless sufficient precautions are observed. For this reason, all fittings and valves used in the presence of the gas must be absolutely free of grease or other foreign matter, including water.

Water and fluorine react in a rather complex fashion; the products are primarily oxygen and hydrofluoric acid. To a lesser extent, hydrogen peroxide, ozone and oxygen difluoride are also formed.

Chlorine, although less reactive than fluorine, still combines directly with almost all the elements. In its elemental state, chlorine is a greenish-yellow gas. The color, in fact, gives chlorine its name (from the Greek *chloros*, meaning "greenish-yellow"). Always found in nature combined with other elements, especially with sodium as the ubiquitous sodium chloride (NaCl, common salt), or as the mineral carnallite ($KMgCl_3 \cdot 6H_2O$), and as potassium chloride (sylvite, KCl), chlorine and the chlorides are essential to man's survival.

One of the highly electronegative elements, chlorine's normal oxidation states are −1, and 1, 3, 5, and 7. In combination with hydrogen or oxygen, chlorine exhibits valences throughout the range −1 to +7 (with the exceptions of 2 and 6, for which no compounds are known).

Considerably easier to handle and store than fluorine—although still requiring suitable precautions—chlorine is highly soluble in water. For example, at 10° C (50° F) one volume of water will dissolve a bit more than three volumes of the gas. In smaller concentrations, chlorine is used all over the world to purify drinking water, making use of the element's germicidal and bactericidal properties.

Chlorine is easily liquefied, either pneumatically or by cooling the gas in a closed container to about −35° C (−31° F) at normal atmospheric pressure. In either instance, the element is highly toxic. Like fluorine, chlorine is encountered as a diatomic molecule rather than as single chlorine atoms.

PRODUCTION METHODS

Both fluorine and chlorine are produced on an industrial scale by electrolysis. In addition, chlorine is sometimes manufac-

tured from chlorides that can be acted on by oxidizing agents, although production by this method yields only a small percentage of the world supply.

Since the most common, and by far the least expensive, raw material for chlorine production is sodium chloride, vast quantities of the substance are used in manufacturing the gas. In the simplest type of reaction, an aqueous solution of sodium chloride is electrolyzed to yield chlorine and a solution of sodium hydroxide:

$$NaCl + H_2O \xrightarrow{+e^-} Cl_2 + NaOH.$$

Special reaction cells are used to obtain chlorine in this way, and special care is taken to prevent the chlorine from mixing with hydrogen gas. Even though hydrogen is not shown in the equation, some is evolved from electrolysis of the water. Furthermore, since these elements combine explosively, utmost consideration is given to keeping them apart.

Fluorine is produced by the electrolysis of a potassium hydrogen fluoride solution in anhydrous hydrogen fluoride. Because of the difficulties inherent in the production and handling of elemental fluorine, its manufacture was quite limited prior to World War II. However, the newly emerging nuclear energy science of the mid-1940s gave impetus to the development of fluorine technology. Today, thanks to the worldwide atomic energy program and its huge demand for the element, fluorine is readily available for many purposes.

The methods by which fluorine is produced today are little different from those used by Moissan in the 1880s. As stated, the gas is a product of fluoride salt electrolysis carried out in special metal or transparent fluorspar containers. The product is stored either as a gas under pressure or as a pale yellow to colorless liquid.

COMPOUNDS AND USES

Of all the chlorides, sodium chloride is by far the most important both from the industrial standpoint and in human physiology. As a raw material, common salt takes part in numerous processes. In the human diet, it is indispensable in maintaining the delicate electrolyte balance in the body.

Ranking close to sodium chloride in terms of importance is hydrogen chloride, better known as hydrochloric acid (HCl) when in aqueous solution. The gas is highly irritating, colorless, and extremely soluble in water. In fact, one volume of water will dissolve more than 500 volumes of HCl. As the anhydride, HCl will not react with many metals. In solution, however, it is one of the primary mineral acids (along with sulfuric and nitric acid), reacting with most common metals to form the respective chlorides. This, in itself, explains in part the industrial importance of hydrochloric acid.

Furthermore, the gastric contents of the human stomach contain HCl in respectable concentration. Indeed, the normal concentration of hydrochloric acid in the stomach is sufficient to attack cloth, a fact attesting to the durability of the stomach lining.

Among the oxychlorides, perhaps the most important are the hypochlorites. Such compounds are able to liberate gaseous chlorine in water, rendering the compounds useful as bleaching agents. Large quantities of these compounds are used in the textile and paper industries for this purpose.

Other notable inorganic chlorine compounds are the salts of chloric and perchloric acids—the chlorates and perchlorates, respectively. These compounds are ready sources of oxygen, and are used in the manufacture of explosives and matches. Sodium chlorate, $NaClO_3$, is an effective herbicide.

The list of organo-chlorine compounds is extensive, especially if all the plastics of which chlorine is a part are named. In this vein, perhaps the best-known compound is polyvinyl chloride, PVC.

In organic synthesis, chlorine plays a major role in oxidation and substitution reactions. Of the latter, a form of synthetic rubber is produced by substituting chlorine for hydrogen in certain organic compounds.

Fluorine is now of paramount importance in organic chemistry, since it has been proposed that this element might be capable of substitution for hydrogen wherever it occurs in organic compounds. This being the case, organo-fluorine compounds could easily number into the thousands.

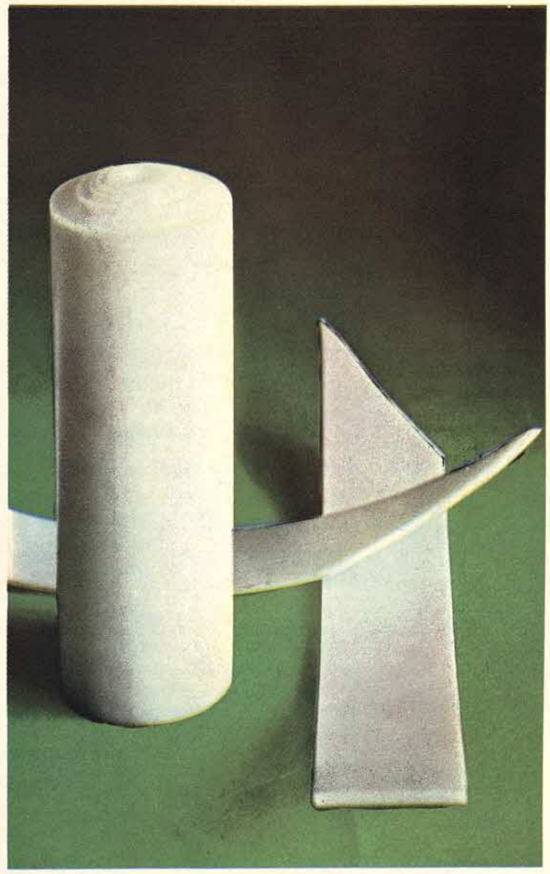
On the everyday level, fluorine's chief acid, hydrofluoric, HF, an inorganic acid, is used to etch the "frosting" on light bulbs. This is the only acid that will react with silica, the primary ingredient in common glass.

Fluorine and a number of its compounds are also used in the production of uranium for the vital nuclear energy industry. This element is now generally available because of the need for fluorine generated by the atomic industry.

More than 100 fluorochemicals of importance are recognized, with the promise of more to come from the most reactive element in the periodic table.

TEFLON — One of the high-temperature plastics, Teflon is a fluorinated organic compound with the chemical name polytetrafluoroethylene. Because of its remarkable antifriction properties it is a valuable dry lubricant. Almost every housewife knows of its "nonstick" qualities in cooking utensils. Furthermore, this compound strongly resists chemical attack, finding use in anticorrosives.

5



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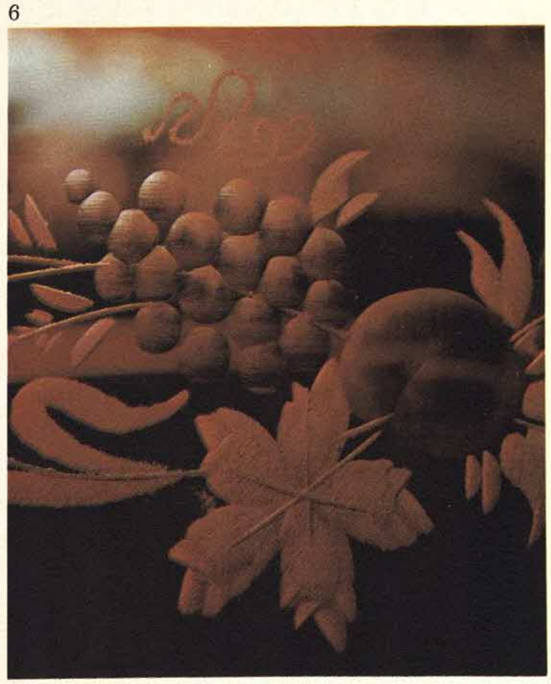


ETCHED GLASSWARE — The most important compound of fluorine is hydrofluoric acid. This is the only acid known that will etch silica, the major component in glass. Thus, frosted light bulbs and some decorated glassware are treated with this acid.

SULFUR | from brimstone to antibiotics

Sulfur (S), the yellow element, has long been a part of man's history; references to the substance are made in Greek mythology and in both Biblical Testaments. Early man used sulfur for a variety of purposes, generally in mystic rites, although some instances of its use in medicine are recorded.

For centuries this element carried with it the unfortunate and undesirable (and certainly inaccurate!) stigma of being a constituent of Hell. This is perhaps understandable in terms of some of sulfur's properties. For example, in regions of volcanic activity, the smell of burning sulfur coupled with an ignorance of natural phenomena fortified the "fires of Hell" myths. Furthermore, since elemental sulfur is easily burned in air, the stories of "fire and brimstone"—"brimstone" meaning "burning stone"—were readily accepted as fact.

Throughout the Middle Ages, alchemists devised numerous theories to ex-

1

SULFUR—In its minerals, sulfur occurs in often beautiful forms. This is a specimen of zinc sulfide, ZnS, or blende.

plain natural occurrences, among them that sulfur was both a "spirit" and an element. In 1772, however, the French chemist Antoine Lavoisier, known as the father of modern chemistry, demonstrated conclusively that sulfur was a specific element. His proof set the stage for the development of sulfur chemistry.

PHYSICAL AND CHEMICAL PROPERTIES

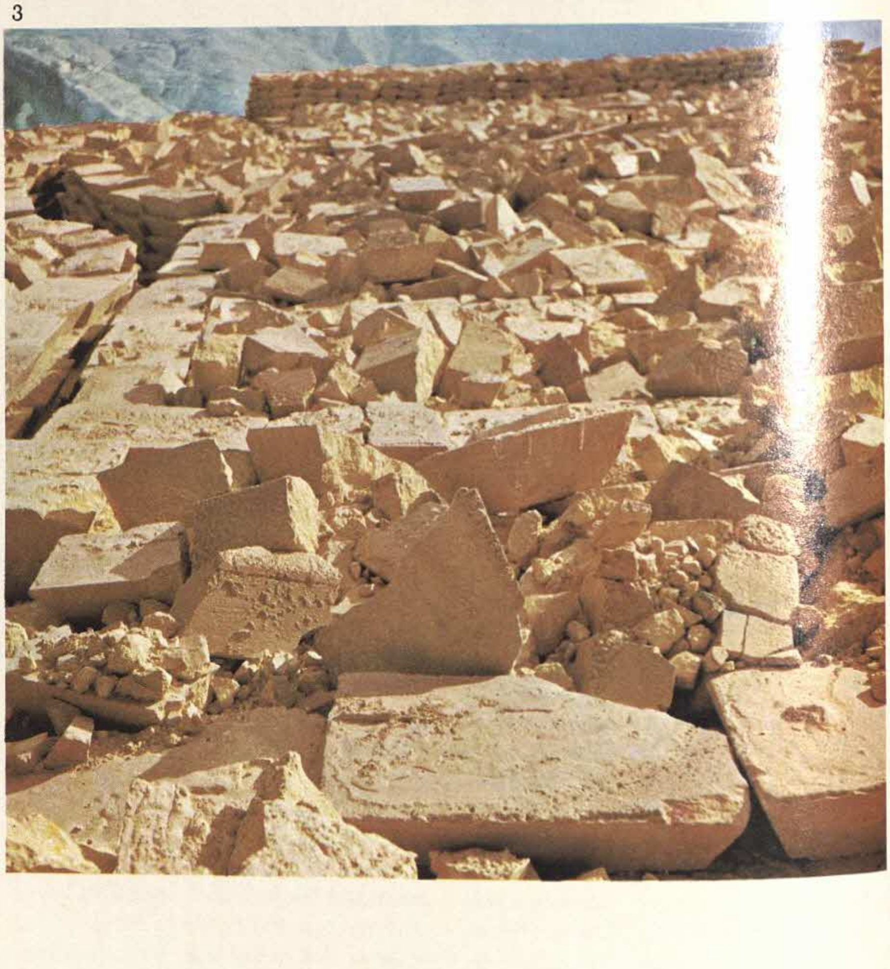
Sulfur, with atomic number 16, occurs most commonly as a yellow solid, either powdery or crystalline in form. Its valences are 2, 4, and 6. It is somewhat unique in that its molecular structure is highly temperature-dependent. For example, above 1,500° C (2,732° F) the

2

COBALT SULFATE — Under the microscope, these crystals of cobalt sulfate, $CoSO_4$, take on a jewellike quality when viewed in polarized light.

SULFUR BLOCKS—Like haphazardly strewn boulders, these blocks of solid sulfur wait for further processing. Once far below the Earth's surface, the sulfur was melted with hot water and pumped into forms to solidify. Sights like this are common in Texas and Louisiana where important deposits of elemental sulfur are mined.

3



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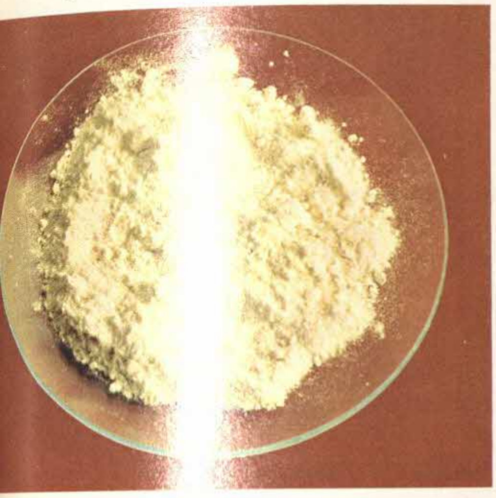


FLOWERS OF SULFUR—Another form of elemental sulfur is obtained by sublimation of sulfur-containing gases. The result is this finely divided, highly pure yellow dust.

element exists in an atomic phase, but at considerably lower temperatures the atoms join molecules. An oxygen-like S_2 molecule can be observed at around 1,000° C (1,832° F). Other combinations of temperature and pressure result in the formation of ring structures or long, branched chains.

While normally solid, sulfur also occurs in several allotropic forms, notably a heavy liquid (in relation to water) and a viscous "plastic" mode. Both can be easily formed by heating solid sulfur. In any case, the element is insoluble in water but soluble in carbon disulfide, CS_2.

Chemically, sulfur is a rather active material, combining with a wide range of other elements at normal temperatures. In fact, vigorous reactions take place at room temperature with the alkali and alkaline-earth metals, and sulfur readily forms compounds with copper, mercury, and silver. In the last instance, the tarnish on silverware is a common example of sulfur's action. If heated, sulfur reacts with additional elements. At higher temperatures, however, some materials are untouched even by boiling sulfur—a property exploited industrially for the handling of sulfur. At the boiling point—444.6° C (about 823° F)—sulfur generates vapors that turn deep red at 500° C (932° F) and a straw yellow at 850° C (1,562° F).

NATURAL OCCURRENCE AND PROCUREMENT

Sulfur is one of the more widely spread elements in nature, occurring both in the elemental state and in a variety of compounds. Of these, the majority are sulfides and sulfates. Sulfur ranks about ninth in abundance in the Earth's crust.

Large and important deposits of elemental sulfur occur in Louisiana and Texas in the United States, and in Mexico. The sulfur in these locations is recovered by a method known as the Frasch process. Essentially, this process involves melting the underground sulfur with superheated water and pumping it to the surface to solidify. Illustration 5 diagrams the mechanics.

Other deposits, especially those in Sicily, Japan, Poland, and the Soviet Union, are mined by conventional means, with the sulfur being concentrated by flotation.

Another source of this valuable element is natural gas wells. Here, sulfur is recovered from the gas by special absorption techniques in the Claus process. Because of the rising consumption of natural gas and other hydrocarbons, this source promises to gain in stature.

COMPOUNDS AND APPLICATIONS

Before discussing sulfur's numerous compounds, the element itself is worthy of further attention. Uncombined, it is a vital material in both plant and animal physiology; sulfur is found in virtually all living things to the extent of about 1 percent by weight. In this respect, proteins and their manufacture require the presence of sulfur atoms; and through an established "sulfur cycle," organisms break down sulfur-containing minerals.

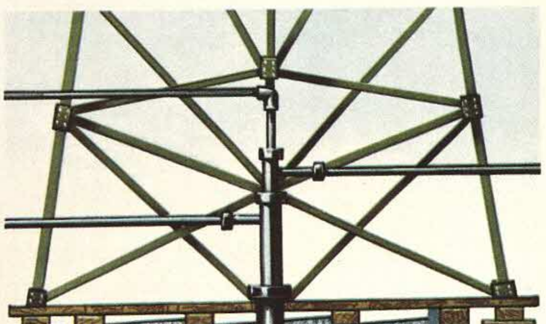
Sulfur's most important contribution to mankind, aside from its physiological aspects, is sulfuric acid, H_2SO_4. It has been said that the production and consumption of this acid is a mark of a society's advancement (philosophical considerations notwithstanding). Sulfuric acid is an extremely strong mineral acid with an affinity for water. In fact, it reacts rapidly with many organic compounds, removing the water to leave a carbon residue. Because this acid reacts vigorously with water with the production of quantities of heat, serious accidents have occurred when a boiling acid-water mixture has erupted into the face of the uninformed. In all cases, sulfuric acid should be added quite slowly to any water, with continuous gentle stirring of the mixture.

This acid has wide applications in numerous industries, including metallurgy, plastics, petroleum, and pharmaceuticals.

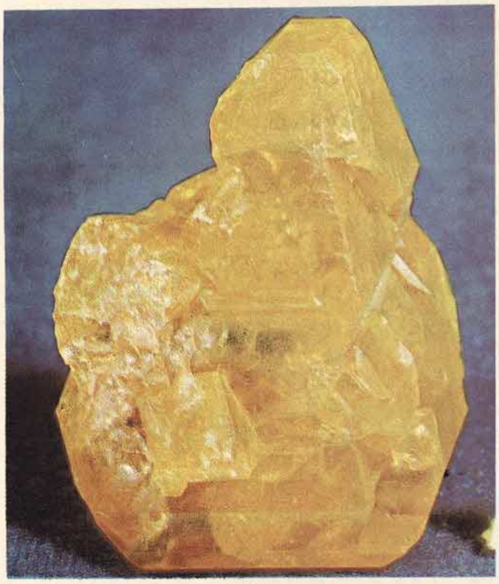
Sulfur's oxides include the dioxide, SO_2, and trioxide, SO_3. Today, the former is recognized as a major pollutant from industry and from the burning of coal in heating plants. SO_2 is a respiratory irritant, but is also an efficient bleaching agent—less active in this respect than

FRASCH PROCESS — Used primarily in the United States, the Frasch process uses superheated water to melt underground sulfur. As the hot water is introduced, the molten sulfur is pumped to the surface to solidify (see Illustration 3).

5



6a



CRYSTALLINE SULFUR—The yellow, translucent mass of crystals in Illustration 6a is a specimen of the rhombic form of sulfur. This form is stable at room temperature. In Illustration 6b, the monoclinic structure has resulted from the heating of the rhombic form.

6b

chlorine. As such, sulfur dioxide is mixed with water to form sulfites, and these compounds are used extensively in the pulp and paper industry. The sulfites are capable of removing the natural "glue" in wood fibers, a sticky material called lignin, leaving cellulose fibers from which paper is made.

Sulfur trioxide, sometimes called sulfuric anhydride, has little purpose except in the production of sulfuric acid. When added to water, the oxide reacts to form the acid:

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

Two other oxides of sulfur, S_2O_3 and SO_4, are known. The sesquioxide, S_2O_3, is formed by adding powdered sulfur to liquid sulfur trioxide at 15° C (59° F). It is a blue to blue-green solid which decomposes slowly into SO_3, SO_2, and S. Sulfur tetroxide, SO_4, a white solid, is prepared by subjecting a mixture of SO_2 and O_2 to a silent electric discharge. In the gas phase, SO_3 consists of monomeric molecules; in the liquid state, it consists of a mixture of SO_3 and S_3O_9 molecules and perhaps others.

With many metals, sulfur forms sulfides. Among the more important are iron sulfide, FeS, a gold-colored, lustrous mineral that proved the undoing of more than one prospector in the American West. Apart from its role as "fool's gold," pyrite (another name for the compound) is a source of mined sulfur. The element is obtained by roasting the mineral.

Other sulfides are brilliantly colored, and are used to make artist's pigments. Cadmium sulfide, CdS, is a beautiful yellow-orange compound; arsenic disulfide, As_2S_2, is an intense red-brown. In the laboratory, hydrogen sulfide, H_2S, with a smell like rotten eggs, is a valuable tool in qualitative analysis. It provides a ready source of sulfur that, in turn, forms sulfides with other elements. Generally, from the color of the sulfide created, the original, unknown element can be determined. In the same way, many elements can be ruled out in H_2S determinations.

In organic chemistry, the list of sulfur compounds includes the mercaptans, the most malodorous substances commonly encountered. For example, skunks occasionally make their presence known by means of these organo-sulfur substances. On the positive side, onions, garlic, and horseradish owe their distinctive aromas and flavors to mercaptans.

In the manufacture of rubber, sulfur plays the important role of increasing the

SOLIDIFIED SULFUR—If sulfur is heated carefully until it becomes a heavy liquid, and the liquid is cooled quickly, another form of the element appears. In this illustration, the solidified liquid, called amorphous sulfur, is seen immediately after cooling on a glass plate.

7

8

PLASTIC SULFUR — Another modification of sulfur's structure is seen in this illustration. Here, the sulfur molecules have formed a polymeric chain. After a time, this form becomes hard and brittle, similar to the "solidified" modification.

elasticity and thermal resistance to breakdown by the process of vulcanization. Thanks to sulfur, mankind now has pharmaceuticals such as the penicillins and sulfa drugs to fight disease and infection. Certain insecticides contain sulfur compounds that aid in controlling infestation of crops. Many dyes are composed of organo-sulfur groups that add color to man's world.

A further major use is as a plant food. Sulfur and its compounds are used both as direct and indirect fertilizers. As indirect fertilizers, sulfur and its compounds have various functions, including the correction of alkali soils, reaction with soil constituents, and release of the nutritional elements.

COMMERCIAL FORMS OF SULFUR

Crude sulfur, or brimstone, on the United States market is 99.5 percent to 99.9 percent pure and free from arsenic, selenium, and tellurium. As shipped, it contains about 50 percent fines (finely crushed or powdered material) with lumps 8 in. or more in diameter. Italian sulfur is marketed in four grades known as best seconds, best thirds, good thirds, and current thirds and ranging in sulfur content from 99.5 percent down to 96.0 percent. Japanese sulfur is usually marketed in the form of cylindrical bars, each containing slightly more than one cubic foot of 99.8 percent to 99.0 percent sulfur and weighing 130 to 150 lbs.

Broken-rock brimstone is sublimed or refined sulfur broken and sold as a mixture of lumps and fines. It has uses similar to roll sulfur.

Colloidal sulfur is sulfur in such small particles that it remains suspended in water. Colloidal sulfur may be prepared by intensive grinding but is usually prepared by chemical means.

Commercial flour sulfur is produced by grinding crude sulfur. Its fineness is 50 percent to 99 percent through a 200-mesh or 99 percent through a 300-mesh sieve. It is used in vulcanizing rubber, in dyes, gunpowder, and insecticides.

Flowers of sulfur (Illustration 4) is sulfur refined by sublimation. It is used in chemicals, in vulcanizing rubber, in insecticides, fungicides, and pharmaceuticals (especially after washing with ammonia to remove all traces of acid).

Lac sulfur, precipitated from polysulfide solutions by sulfuric acid, contains up to 45 percent calcium sulfate. Its uses are mainly pharmaceutical.

Precipitated sulfur is precipitated from polysulfide solution by hydrochloric acid and is washed free of calcium chloride. Its uses are mainly pharmaceutical.

Roll sulfur is refined sulfur cast into convenient sizes, and is also known as stick or cannor sulfur. Its uses are chemical, burning for curing, fumigating, and preserving or bleaching effects.

GOLD | the metal with a fascinating history

Gold—known to the chemist as Au—may have been the first metal recognized and sought by primitive man. The allure and legendary fascination of gold is apparent throughout recorded history, which the bright yellow metal helped to shape. In recent times the lure of gold has set off gold rushes, such as those in California in 1849 and in the Yukon Territory of Canada in 1897.

Gold is both rare and valuable. It is rare in that the crust of the Earth contains less of it than of many other heavy metals with an atomic number near that of gold, 79. It is valuable because it does not oxidize in the air, even at high temperatures, and because common acids do not attack it. When it has been polished, it stays shiny indefinitely. Gold was first used for jewelry, then for coins, and later as a base to insure the convertibility of currencies in circulation. Gold also has wide-ranging technical applications.

GOLD IN NATURE

Gold is found naturally in lode (primary) deposits and placer (secondary) deposits that sometimes contain as much as 15 percent or more silver. Gold also occurs in deposits with copper and tellurium and is produced as a by-product of the refining of these elements. In lode deposits, gold is embedded in the quartz present in volcanic or metamorphic rocks. In placer deposits, gold dust or nuggets are found in sand that has been worn off rocks and carried away by rivers or streams. Both types of deposits are commercially important. Among the largest producers of gold are the Republic of South Africa, the Soviet Union, Canada, the United States, and Australia. In ancient times, gold was extracted from deposits in Nubia, Asia Minor, and India. The Romans imported gold from the Iberian peninsula. Between Biella and Ivrea in northwest Italy are the remains of a huge gold mine in which a decree of the time banned contractors from employing more than 5,000 slaves at one time. More than half of the world's gold production now comes from the Republic of South Africa.

THE USES OF GOLD

Gold has been used to coin money since ancient times. When the money in circulation increased above the amount of gold available for new coinage, it became necessary to turn first to other metals and later to paper, guaranteeing the value of such currency by a gold backing. Most of the gold was put into a monetary reserve, where its value depends precisely on not using it except as a means to settle monetary debts between nations.

NATIVE GOLD—Gold is found naturally in the form of thin layers of varying thickness (as shown here), as fine dust, or in nuggets. Gold is widely dispersed in the Earth's crust.

1

GOLD INGOT—The final stage of gold extraction and refining is the ingot, which is cast in a clay mold. An ingot usually weighs about 70 kg (about 155 lb) but occupies little space (about 3 liters or about 185 in.^{3}) because it has a high density. The ingot shown is crude and would undergo further working. Ingots in the gold reserves are more highly refined in general and have a smoother surface. Banks sell small ingots for hoarding. A completed ingot is covered with a varnish, which cannot be removed unless removed completely, and is stamped with seals. When sealed gold of this kind is traded, the ingot does not have to be weighed again because its weight and purity are guaranteed by the issuing bank.

2

GOLD SEAM—A particularly rich seam of gold-bearing quartz in a Transvaal mine. These seams cover a vast area and represent a massive reserve of the valuable metal that was one of the first to attract man's attention.

3

4a

4b

EXTRACTION OF GOLD-BEARING QUARTZ— Miners bore into gold-bearing quartz with a pneumatic drill. The hole is filled with an explosive which, when detonated, breaks off a large amount of material in very small fragments. The galleries of the mines in the Transvaal stretch for hundreds of miles. The deepest goes down 3,000 m (about 2 mi), the deepest man has penetrated into the Earth.

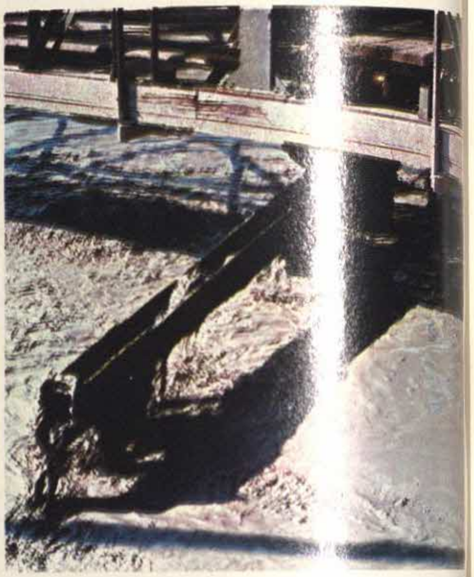
CRUSHING MILLS—The gold-bearing quartz, extracted in small fragments from the mines, is sent to crushing mills, where steel balls operating under water reduce the ore to a mush. The small particles of gold in the quartz are thus freed and left suspended in the mush. Illustration 5 shows a crushing mill just after it has been filled with water. After the crushing process, the water takes on a grayish color because of the mush that has been formed. The product of the crushing mills is then separated by an amalgamation technique.

5

7

EXTRACTION BY AMALGAMATION—Illustration 7a shows the quartzite ready to be separated from the metal. This system is used to treat quartzites with at least 10 g of gold per ton. Gold is extracted from lode deposits with a content as low as 3 g per ton.

a



6

CYANIDING—The mush, which has been passed across plates of amalgamated copper, still contains recoverable gold. Illustration 6a and 6b show the mush after amalgamation, when it is concentrated and then passed on to the tanks for cyaniding. In this process, the mush is treated with large quantities of a very dilute, water solution of sodium cyanide. The sodium cyanide attacks the gold, turning it into a complex solution by the reaction:

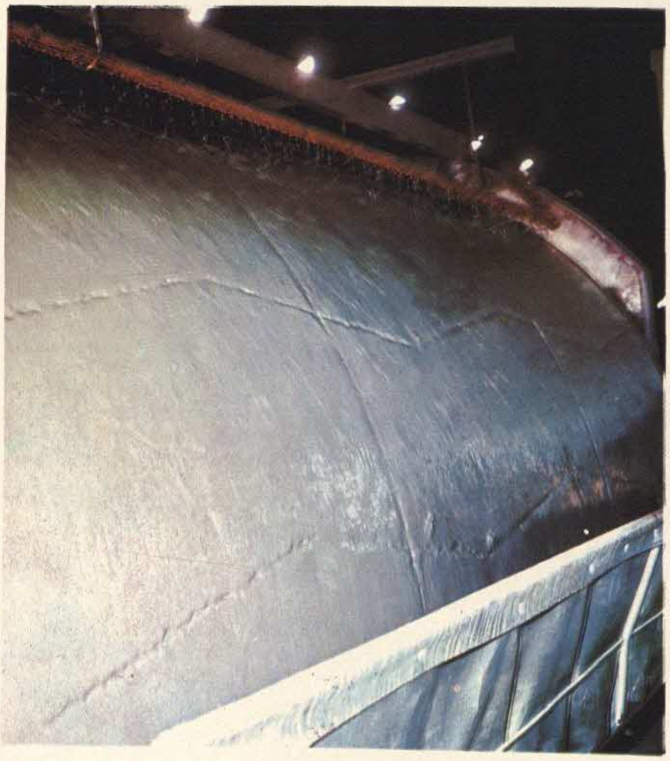
$$4Au + 8NaCN + 2H_2O + O_2 \rightarrow 4NaAu(CN)_2 + 4NaOH.$$

The reaction is initiated by the oxygen dissolved in the water, and the reaction takes place rapidly. The result is the formation of a solution of double cyanide of sodium and gold, from which it is possible to precipitate gold through the use of metallic zinc:

$$2NaAu(CN)_2 + Zn \rightarrow 2Au + Na_2Zn(CN)_4.$$

The gold precipitated in this way contains other metals as impurities and has to be further purified. Cupellation separates out all the remaining impurities, apart from silver, which is removed by the process of quartation. Silver is added to the gold until it forms an alloy that is three-quarters silver and one-quarter gold—hence the name, quartation. Nitric and sulfuric acids attack this particular alloy, leaving a pure gold residue.

a

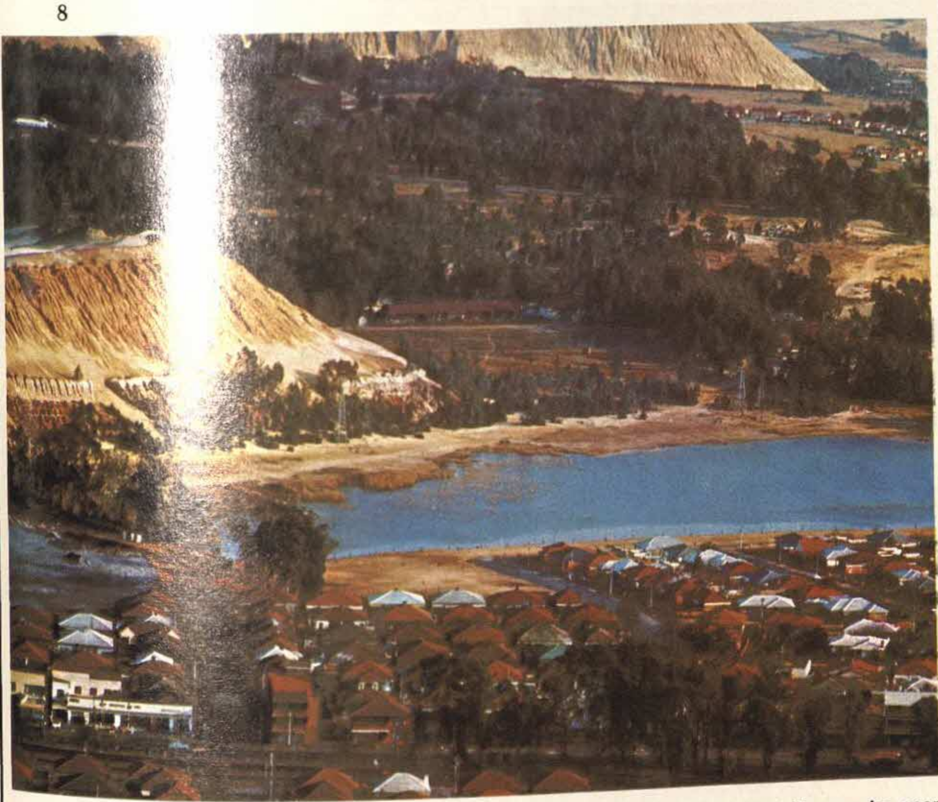


b

In Illustration 7b, the ground mush is pushed across plates of amalgamated copper (copper alloyed with mercury) by a screw-shaped pump. The mercury in the amalgam is alloyed with most of the gold present in the mush. The process requires some time because all of the mush must come in contact with the amalgamated copper plates. Afterward, the plates are taken out of the tank and the amalgam is scraped off the surface. The amalgam is then heated so that the mercury evaporates and the gold is recovered.

b

8



HILLS OF WASTE MATERIAL—The landscape in the Transvaal is characterized by the shape of the hills of crushed rock from which gold has been extracted. These hills can be seen just outside Johannesburg, a city under which are many mine galleries.

Because gold is a soft metal similar to tin and copper, it is hardened for the purposes of coinage by alloying it with other metals, although some pure gold coin has been minted. The amount of gold in an alloy is expressed in carats in a range of from 0 to 24. Pure gold is 24-carat gold; the grade of the alloy expressed in carats represents the amount of the metal expressed in 24ths. Eighteen-carat gold is 18/24 gold, or 750 parts in 1,000. Gold alloyed with copper produces red gold; with silver, yellow gold; and with nickel, platinum, or certain other metals, white gold.

A large amount of gold, usually in the form of an alloy, is used for jewelry. Gold has technological uses that utilize its chemical stability. Large amounts are used for dental fillings and for gilding, whether as decoration or to protect other materials from corrosion. Because gold has high conductivity (although not as high as copper or silver), gold plating is widely employed in the field of electronics, where it is used for the terminals of transistors and microcircuits. Such terminals require perfect electronic contact, even at low voltages.

Gold is valuable as a component in a wide range of equipment because it is malleable—gold leaf can be made thinner than 0.001 mm (about 0.00004 in.). Because of its lower cost, gold is often used in place of platinum where an inert metal is required, even though gold is less inert than platinum.

CHEMICAL PROPERTIES

Gold is not attacked by acids except for certain mixtures of nitric and hydrochloric acid, iodic acid, and selenic acid. It is also attacked by cyanides in the presence of oxygen in water solution. Gold keeps its brilliant sheen because oxygen does not attack gold even when the surrounding air is hot.

The metal behaves monovalently or trivalently; thus there are two series of gold compounds, aurous and auric. The most important compound in the aurous series is sodium aurocyanide, $NaAu(CN)_2$. Aurous chloride, sulfide, iodide, and fluoride are also known. The best-known compounds of the auric series are the chloride, $AuCl_3 \cdot 2H_2O$; the oxide; the hydrate; and the sulfide.

Gold can be analyzed by precipitating the metal from its compounds through reduction. To determine the gold content of alloys containing silver, copper, and nickel, the alloy may be rubbed on a flint. The trace of metal left on the flint is then treated with nitric acid, which dissolves the other metals but leaves the gold intact. Comparing this trace with traces of alloys with known gold content completes the analysis. Modern methods of gold analysis include spectroscopic and x-ray fluorescence techniques.

BORON | an element in a white cast

In Death Valley, California, a bright and scorching sun beats down on vast areas that reflect a dazzling white. Rich in history, the valley takes its name from the fate of a party of "Forty-niners" who perished there; but it is even richer in minerals—particularly the white salts that are a major source of an important element: boron.

2

COLEMANITE—This is a prismatic, monoclinic mineral with the formula, $Ca_2B_6O_{11} \cdot 5H_2O$. One of the most important minerals for the extraction of boron, colemanite is found in great abundance in California's Death Valley and in Nevada.

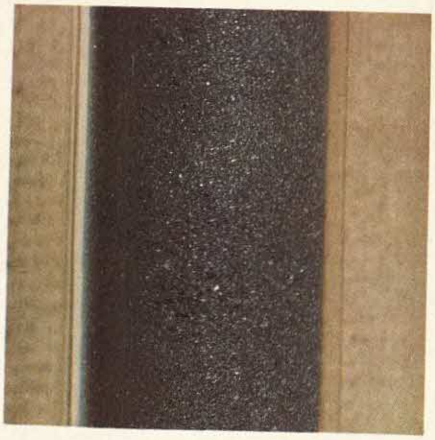
In the periodic table of elements, boron is the lightest member of the third group. It has chemical properties similar to those of aluminum, indium, and thallium (also in the third group), and special properties that it has in common with silicon in the fourth group. Boron has a minimum specific gravity of 2.34 and its melting and boiling points, above 2,200° C (3,992° F), are much higher than those of other elements in the third group.

BORON IN NATURE

There are about 70 minerals in which boron is found, but only a few of these minerals are important for the extraction and exploitation of the element. Boron appears most frequently in borax (tincal), $Na_2B_4O_7 \cdot 10H_2O$; natural boric acid (sassolite), H_3BO_3, and in colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$. Boric acid, which is widely used as a disinfectant for the eyes, is found mixed in the water vapor of volcanic fumes. The presence of boron in many other minerals is of interest only as a curiosity and as a reason for studying its geochemical behavior. For example, minute quantities of boron are found in tourmaline and seawater.

BORON—This amorphous, dark-colored form of boron is produced by reducing boric oxide with aluminum dust.

1



DISCOVERY AND PROPERTIES

Boron was first isolated by Sir Humphry Davy and, independently, by Gay-Lussac and Thénard in 1808. In both cases, the new element was isolated by heating boric oxide (boric anhydride), B_2O_3, with metallic potassium. There are practically no applications for boron in its elementary state because of its high affinity for oxygen. Boron melts at 2,300° C (4,172° F) and, if heated further at ordinary pressure, will not boil because it sublimes long before reaching the boiling point. At 2,550° C (4,622° F) it sublimes so quickly that it is used up almost immediately.

Boron has two stable isotopes that absorb neutrons differently; in particular, the isotope of mass 10 has the greatest absorption of neutrons. Adding boron to the material in a nuclear reactor will stop the reaction; the graphite used to control neutrons requires less than one part of boron for every 10 million parts of carbon. Boron is present in graphite as a carbide that melts well above 2,400° C (4,352° F) and only sublimes above 3,500° C (6,332° F). It is impossible to eliminate boron by heating, which volatilizes most impurities.

Elementary boron can be isolated by heating the chloride, BCl_3, at 1,100 to 1,200° C (2,012 to 2,192° F) in the presence of hydrogen, which separates the chlorine from the molecule. It is also isolated from the anhydride by using oxygen-hungry reducer elements, such as magnesium and aluminum, by a process similar to the heat treatment of aluminum or calcium. Boron is almost exclusively trivalent and forms various compounds with hydrogen, carbon, oxygen, and other elements.

It also shows a very marked affinity for the halogens; with them, boron forms compounds made up of molecules with a planar structure in which the very small B^{3+}, which has an ion radius of 0.20Å, is surrounded by three Cl^- spheres whose ion radius is about nine times greater (1.81Å). The combination of

boron with the halogens takes place spontaneously through a very lively combustion reaction. The fluoride is gaseous and catalyzes various organic reactions, including alkylation and polymerization. Boron hydride and lithium undergo a double exchange reaction that leads to the formation of a cyclic compound, diborane. The reaction is as follows:

$$BF_3 + 3LiBH_4 \rightarrow 3LiF + 2B_2H_6.$$

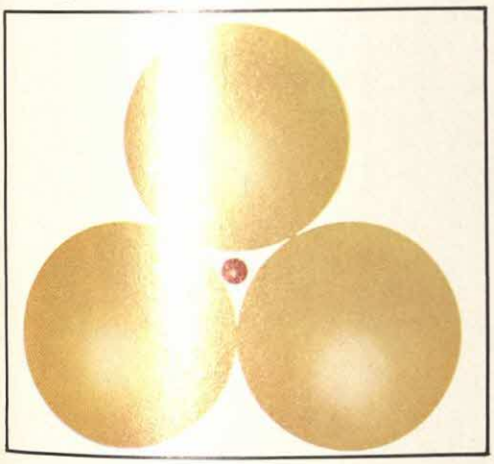
The boron compound, boron nitride (BN), which is almost as hard as diamond, is formed by direct combination of the elements. It has a very high melting point and is an excellent electrical and thermal insulator; at ordinary temperatures, it has a hexagonal structure rather like that of graphite. But at very high temperatures and pressures, the structure of boron nitride is transformed into a cubic modification in which the atoms are closer together. It is in this modification that boron nitride becomes hard as diamond. But whereas boron nitride is stable at low temperatures and pressures, diamond turns into graphite as the temperature increases.

Boron, which has a high degree of affinity for water, decomposes in water at high temperatures and links up with oxygen. The fundamental oxygenated compound is boric anhydride, B_2O_3, a glassy-looking hygroscopic substance from which various acids are derived, such as orthoboric acid, H_3BO_3 (also called boric acid or sassolite), which crystallizes into white, lustrous scales with a low solubility in water, about 3 percent at 20° C (68° F). Boric acid distills with water vapor, which explains why it is found in the superheated vapor of the Tuscan steam jets from which it is extracted. At 100° C (212° F), orthoboric acid loses one water molecule to give metaboric acid; and at 140° C (284° F), it changes into tetraboric acid according to the following reactions:

$$H_3BO_3 \xrightarrow{100^\circ} H_2O + HBO_2;$$

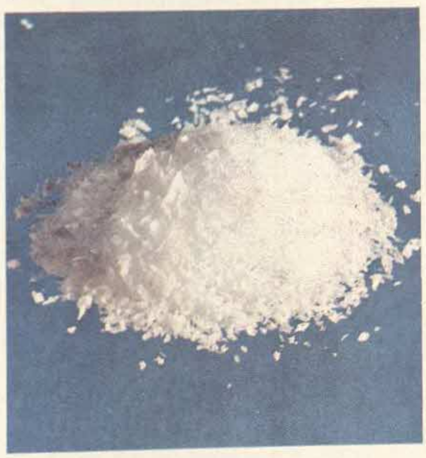
$$4H_3BO_3 \xrightarrow{140^\circ} 5H_2O + H_2B_4O_7.$$

3



BORON TRICHLORIDE—The small boron ion is surrounded by three halogen ions. All boron halogenides have a planar structure.

4



SCALES OF BORIC ACID—Boric acid, H_3BO_3, is only moderately soluble and crystallizes into translucent scales.

Borax is the sodium salt of tetraboric acid with the formula $Na_2B_4O_7 \cdot 10H_2O$. The large quantity of crystallization water is lost when heat is applied. At 80° C (176° F) it drops to only 5 water molecules, and at still higher temperatures it disappears altogether. The salt dissolves in the crystallization water and, when this evaporates away with the increasing temperature, the salt melts and breaks into $2NaBO_2$ and B_2O_3. The boric oxide formed in this way dissolves the metallic oxides; it is, therefore, used to clean the metal surfaces in autogenous welding or silver soldering.

Pure, molten borax is a transparent white. But if ions of other elements are added, the borax takes on colors that are so intense that the substances dissolved in the borax can often be recognized with certainty. Borax is widely used in the glass industry as a flux for quartz. Glass is made up principally of silicon dioxide (quartz), whose melting point is very high, about 2,000° C (3,632° F). An addition of borax lowers this melting point, turning the mixture into a substance that melts above the temperature of 800-850° C (1,472-1,562° F). At this temperature, the mixture is so viscous that it behaves much like a solid. Because borax mixes easily with glass and ceramic substances, lowering their melting point to a desired level, it is also useful for preparing enamels—kinds of glass with a low melting point that have been mixed with ceramic substances and are used to protect metals from corrosion. If these substances are to stick to the metal after cooling, both metal and enamel must have the same coefficient of expansion.

An important oxygenated compound of boron is sodium metaperborate, whose formula is $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$. This compound is stable when solid; but if dissolved in water and heated slightly, the molecules of sodium metaperborate release hydrogen peroxide. This property makes sodium metaperborate useful as a bleach in many preparations, especially in laundry detergents.

THE CYCLIC COMPOUNDS

Boron combines with hydrogen to form a series of compounds that are called boranes or boron hydrides. The most important of the boranes is the first term, diborane, which has the formula, B_2H_6. As the number of boron atoms in the series grows, the melting and boiling points rise as in hydrocarbons. Heating the solid compound, $BH_3 \cdot NH_3$, produces a liquid, $B_3N_3H_6$, called borazole. It has a structure similar to that of benzene. As with the analogous aromatic hydrocarbon, borazole dissolves fats easily.

LEAD | one of man's first metals

The history of lead (Pb) goes back to early antiquity. It is mentioned in the Bible, in the Song of Moses (Exod. 15:10): "Thy spirit blew, and the sea overwhelmed them; they sank like lead in the turbulent waters." The early Romans were expert at working lead, using it to make water pipes and the standards bearing their military insignia.

Despite its long history, the element lead came into common usage only after the growth of industry, especially reaching its stride in the twentieth century. It is ranked—after iron, aluminum, copper, and zinc—among the metals most widely used today. The chief producers of lead are the United States, Canada, Australia, Mexico, and Peru. In its natural state, lead occurs as a minor component in dolomite and limestone. Deposits of other metals, such as copper, silver, zinc, and gold, occasionally contain lead.

PRODUCING LEAD FROM GALENA

The most common lead ore is galena, or lead sulfide. In extracting lead from galena, the sulfur must first be removed from the galena. In this process, it is essential either that the sulfur combine with oxygen or that the lead be oxidized, then reduced successively. Thus, there are two basic processes: the first is called roasting; the second is known as the roasting-and-reduction process. The first is similar to that used in extracting iron from pyrites, in which the chemical reactions involved are:

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$

These reactions take place at a temperature below 700° C (1,292° F). At higher temperatures, up to about 1,000° C (1,832° F), coke (carbon) can be added to reduce the roasting products to elemental lead. Both operations occur in the same reaction chamber.

The second phase—reduction—is accomplished with coke and is, therefore, very economical. The addition of silica transforms the sulfate into lead silicate: $2PbSO_4 + 2SiO_2 \rightarrow 2PbSiO_3 + 2SO_2 + O_2$. Chalk and coke are added later. The coke

1

GALENA, THE MOST IMPORTANT LEAD ORE—The most common lead-bearing ore is galena (PbS), a lead sulfide (Illustration 1a) that has many valuable properties. It is a semiconductor—a substance having an electrical conductivity quotient halfway between that of metals and that of insulating materials. When properly treated, galena can be used to rectify alternating electric current; that is, if the voltage is not too high, galena will allow the current to pass through in one direction only. Because of this property, galena was once used in radio receivers to demodulate Hertzian waves. Galena has a very high specific gravity: about 7.5. In thick layers, it is opaque to ordinary light, and transparent to infrared rays; in thin layers, it is transparent to ordinary light and has a high index of refraction: 3.9—higher than that of most known substances. When purified and used to strengthen glass, galena provides a high index of refraction and a high specific gravity. Glass reinforced with large quantities of galena is used as a shield against nuclear radiation, particularly gamma radiation.

Other important lead-bearing ores are anglesite ($PbSO_4$, Illustration 1d) and cerussite (PbO, Illustration 1h). Rare lead-bearing minerals are crocoite (Illustration 1b); phosgenite (Illustration 1c), wulfenite (Illustration 1e), bournonite (Illustration 1f), and meneghinite, shown crystallized with sphalerite (Illustration 1g).

a

b

c

d

is partially oxidized and forms carbon monoxide, which then reduces the lead oxide and the silicate:

$$PbO+CO \rightarrow Pb+CO_2$$

$$PbSiO_3+CO+CaO \rightarrow Pb+CaSiO_3+CO_2.$$

A third process—precipitation—consists of treating the lead sulfide with iron oxide and coke in a blast furnace. The carbon reduces the iron, which then removes the sulfur from the galena and leaves the lead in its elemental state:

$$PbS + Fe \rightarrow Pb + FeS.$$

These three extraction processes act in a similar way on other minerals found with galena—minerals that cannot be completely separated from galena during pulverization. Thus, the lead produced contains impurities that may themselves be valuable; these impurities are copper, antimony, arsenic, and bismuth. Silver may also be present.

Lead is often purified by smelting, which separates from it many impurities in the form of solid residues, which are oxidized and removed. In some cases the major component of the slag is antimony, and because this metal forms a useful lead alloy it is often left in the extracted metal. A very pure type of lead can be produced by electrolysis.

CHEMICAL PROPERTIES

The valence of lead is +2 or +4; therefore, two series of compounds exist: plumbous and plumbic. Solutions of lead salts, when treated with a strong base, cause lead hydroxide $Pb(OH)_2$ to precipitate; lead hydroxide has a slightly alkaline reaction.

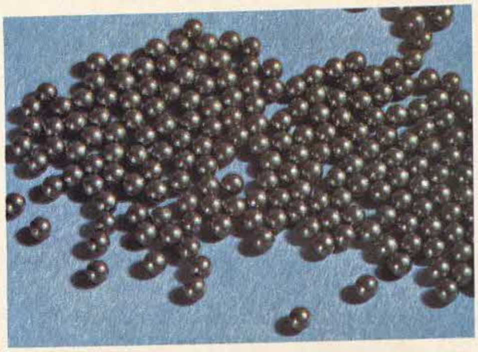
In addition to litharge (lead monoxide) and red lead, another type of lead oxide, the dioxide PbO_2, has a slightly acid reaction. Halides are commonly found among lead salts and include chloride ($PbCl_2$); basic chloride ($PbCl_2 \cdot 7PbO$), which is used in paint as Cassel yellow; lead tetrachloride ($PbCl_4$), and plumbate chlorines. The fluoride and iodide, which have limited uses, are also in

g

e

f

h



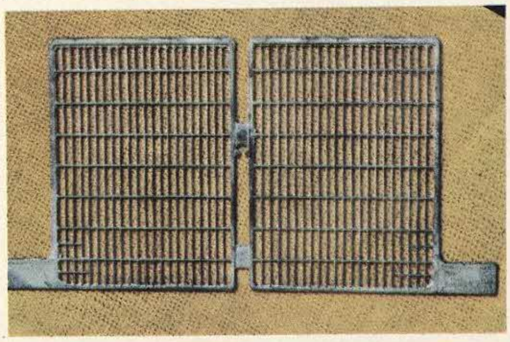
2e

2a

2b

2f

2c



2d

2g

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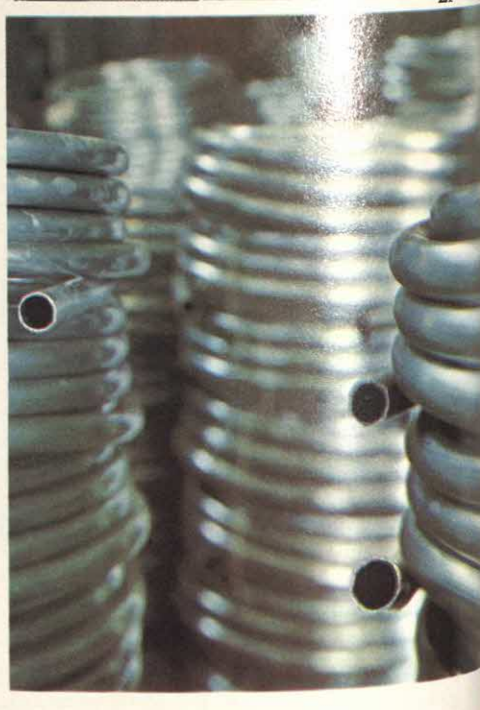
2i



THE USES OF LEAD—Lead is used in alloy form as well as in its elemental metallic state. A 15-25 percent antimony content in lead gives it considerable hardness. This alloy has a low melting point and lends itself well to the manufacture of type (Illustrations 2a, 2b).

The manufacture of battery plates (Illustration 2c) accounts for much of the world's consumption of lead. Although batteries can be made with other metals, lead is widely used because it is so economical.

Lead compounds have many uses. Powdered litharge (PbO, Illustration 2d) is used in glassmaking, ceramics, pharmaceuticals, and adhesive plasters. Also important is saline oxide, or red lead (Pb_3O_4), used especially in manufacturing antirust paints. Red lead also assists drying, especially if the paint base is linseed oil; and most structural iron parts, as in building and bridges, are covered with a coat of red lead before paint is applied.

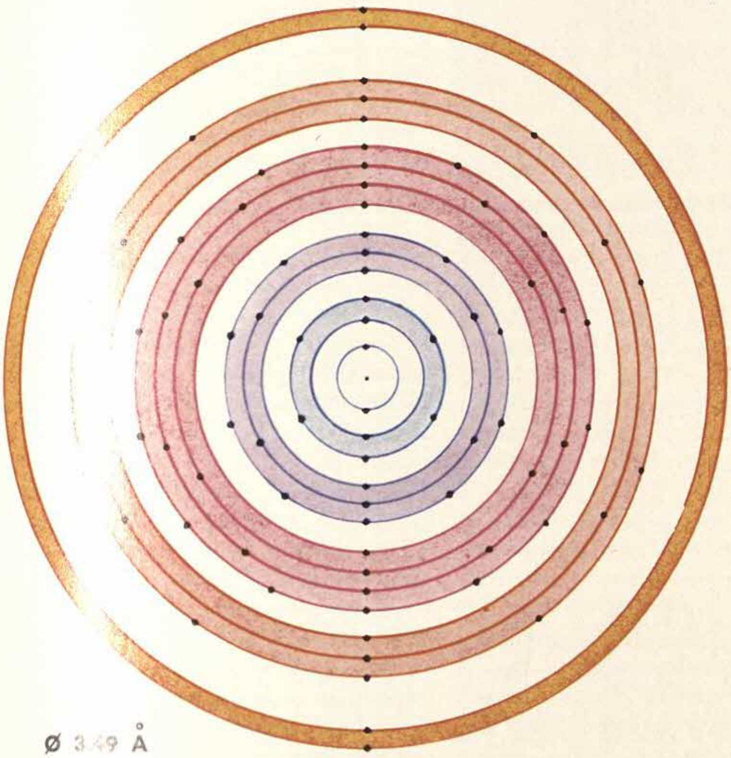
Another useful lead compound is basic lead carbonate, or white lead, a white powder once widely used as an ingredient in paint because of its excellent covering properties. Due to the hazard of poisoning, however, the use of lead carbonate has become limited. In time, white lead paint darkens as traces of lead sulfide form within it. Many old paintings were executed with white lead paint and have darkened with age; such paintings must be treated to restore their original colors. The presence of white lead in a painting can be confirmed by x-rays. Modern copies of old masters are usually painted with organic or inorganic lead-free pigments.

Because of its exceptional hardness, lead-arsenic alloy is used in the manufacture of shot (Illustration 2e). Lead is also used to add weight to artillery projectiles because its high density assures greater powers of penetration and low air resistance.

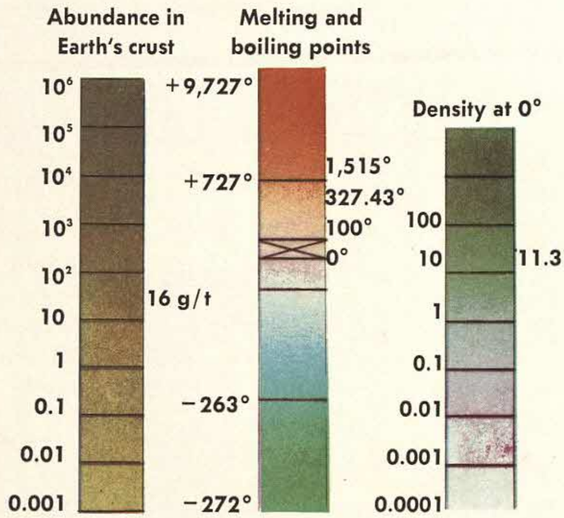
Lead shields help guard against nuclear radiation and X-rays. All types of radiography equipment contain lead shielding; moreover, the operator's hands and body are protected by rubber clothing reinforced with lead (Illustrations 2f, 2g). Radioactive substances are manipulated behind shields built of lead bricks (Illustration 2h shows the lead-lined door of a nuclear reactor).

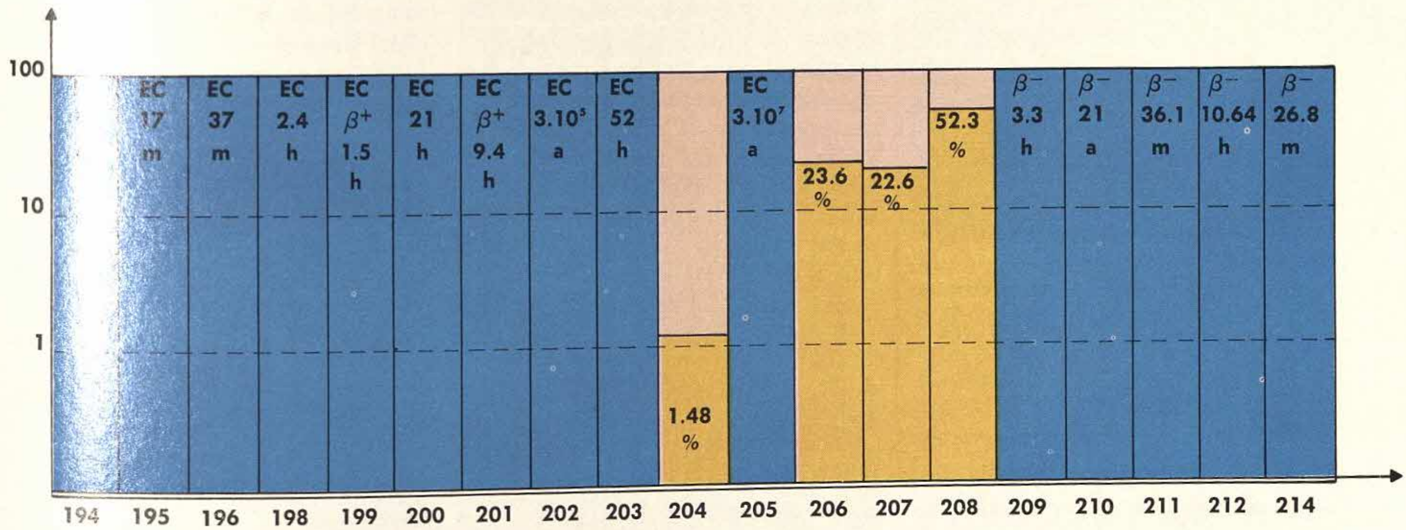
Because it is so soft, lead is still widely used in the manufacture of pipes (Illustration 2i). Lead pipe is often used in houses and industrial applications, where pipe must be bent and twisted continually. Such pipes present no problem in carrying sewer water, but drinking water tends to dissolve them because lead is soluble in water having a low salt content. Rainwater, for example, is not only poor in salts, but is rich in oxygen and carbon dioxide, which again increase the solubility of lead. If the water comes from a spring, thereby having a high carbonate and sulfate content, lead pipes develop a protective coating of basic lead carbonate and sulfate, which prevents the lead from dissolving. And finally, pure lead is used as a sheath for electric cables, although these are being gradually replaced by plastic materials.

ELECTRON CONFIGURATION, ABUNDANCE IN THE EARTH'S CRUST, MELTING AND BOILING POINTS, DENSITY, STABLE AND UNSTABLE ISOTOPES OF LEAD



Ø 3.49 Å





evidence. Halogen compounds are less soluble in cold water with the increased atomic number of halogen chemically combined with lead. Other lead salts are the sulfate, nitrate, and carbonate, or white lead. Lead acetate, $Pb(C_2H_3O_2)_2$, is produced by dissolving lead oxide in acetic acid, forming sweet-tasting crystals known as "sugar of lead"—a deadly poison.

All lead compounds—and lead itself—are highly poisonous. Lead poisoning is known as "saturnism," after the planet Saturn, which was associated with lead in alchemy and astrology. Lead poisons slowly and cumulatively; even the smallest quantity consumed will consolidate with any lead already in the body. Additional doses eventually cause death. Industries using lead avoid chronic lead poisoning by alternating employees who handle the metal. Lead is poisonous in contact with food, or even with substances like toothpaste that are swallowed (lead was at one time present in an alloy used in the manufacture of toothpaste tubes, a practice now illegal—as is the use of lead as a substitute for tin). Lead poisoning often occurs accidentally in young children who ingest lead-containing paint from furniture, woodwork, or toys.

Two important organic compounds of lead are tetraethyl lead $Pb(C_2H_5)_4$ and tetramethyl lead $Pb(CH_3)_4$. Both are used as gasoline additives because of their antiknock properties; these compounds have specific gravities of 1.625 and 1.995, respectively.

SILVER | the metal that makes photography possible

The element silver (Ag), though discovered after gold, has been known to man since ancient times. Silver ornaments have been found in ancient Iberian tombs dating from the Bronze Age.

1

ORNAMENTS AND COINS—Silver has been used since ancient times to make ornaments (Illustration 1a) and coins. The coins shown date from 281-238 B.C. (1b, Magna Graecia; reverse side, 1c); 290-240 B.C. (1d, 1e, Roman Republic); and 89-54 B.C. (1f, 1g, Roman Republic).

In its native state, silver is found in moderate quantities in Spain, Iran, Mexico, India, and China. The silver mines in Nubia and Ethiopia were well known to the ancient Egyptians, and those in Asia Minor, Attica, and Spain were heavily exploited during the Greco-Roman period. After the discovery of America, the Spanish colonies in Central and South America sent large quantities of silver to Spain and Europe.

Native silver is found in cubic crystals generally forming dendritic aggregates or fibrous masses. Silver ores are almost always found close to copper, gold, mercury, and lead ores. The most important silver ores are argentite (Ag_2S), pyrargyrite ($AgSbS_3$), proustite ($AgAsS_3$), and silver chloride ($AgCl$), which is also called horn silver or cerargyrite.

Mexico, the United States, Canada, Peru, the U.S.S.R., and Australia have produced the greatest quantities of silver in recent times.

EXTRACTION AND REFINING

Only one-fifth of the silver produced comes from silver ores; most silver is obtained as a by-product of copper and lead mining. Galena (PbS) contains up to 1 percent silver. Special processes are used to extract silver from silver-bearing lead; one widely used extraction process is the Parkes method, which is based on distributing a solute between two fairly unmixable solvents. Lead and zinc are mutually insoluble at temperatures below 400° C (about 750° F), while silver is much more soluble in molten zinc than in molten lead; it can thus be extracted from lead after being smelted with zinc. A mixture of silver-bearing lead is smelted after 2 percent of zinc is added. The molten mass is stirred until the liquid zinc containing all the molten silver and little of the molten lead collects on the surface. The zinc and silver are then skimmed off and subjected to electrolysis, using the silver as an anode. During electrolysis, zinc is deposited on the cathode while the anode is being consumed and the slime containing lead and silver (70-80 percent) is deposited on the bottom of the cell. This mass is then tested or assayed in a cupel. The process consists of enriching the mixture with Pb-Ag and smelting it in a reverberatory furnace, the bottom of which is porous. A current of air is introduced during smelting to oxidize all the lead into litharge (PbO), part of which is then removed and part absorbed by the porous bottom of the furnace. The silver left in the cupel is 95-98 percent pure. Another way to separate the zinc-silver alloy is through distillation. The more volatile zinc is distilled off, leaving the silver.

Another extraction process is the amalgamation process, used to recover silver from the anode slime left over in copper refining. The impure silver contained in this slime is treated with mercury to separate it from the other elements by dissolving it and forming an amalgam. The amalgam is then distilled in iron retorts to separate the more volatile mercury from the silver, which is left clinging to the iron.

Silver is refined by electrolysis. A cell containing a solution of nitric acid and silver nitrate is used; the silver to be refined acts as the anode, while the cathode is a thin plate of pure silver. During electrolysis the silver on the anode dissolves and is redeposited on the cathode. Impurities such as copper are left in the solution, while gold and platinum precipitate as anode slime.

PHYSICAL PROPERTIES AND USES

Silver is a bright, white metal second only to gold in ductility and malleability. Of all elements, it is the best conductor of electricity and heat, although the high cost of silver precludes wide exploitation of these properties. One of the noble metals, silver does not undergo any change in the presence of oxygen, although it tarnishes when in contact with air. This is because traces of hydrogen sulfide attack it, forming a black film of silver sulfide (Ag_2S).

Silver is used to make plate, expensive tableware, and coins. It is not used in its pure form because it is too soft, but when alloyed with copper it becomes very hard-wearing. Silver alloys are named according to the parts of silver contained in a thousand parts of the alloy. Silver is also used to coat other

less noble metals (silver plate); silver-plating may take place in a galvanic cell, using the object to be plated as the cathode, a sheet of silver as the anode, and a solution of a complex silver salt, such as potassium argentocyanide, $K[Ag(CN)_2]$, as the electrolyte. Chemical silver-plating is accomplished by treating ammonia solutions of silver salts, which thus contain the complex ion $[Ag(NH_3)_2]^+$, with mild reducing agents such as glucose. In this way, a compact layer of silver is gradually deposited.

CHEMICAL PROPERTIES

Because silver is one of the noble metals, it does not dissolve in nonoxidizing acids such as hydrochloric acid (HCl). It does dissolve, however, in oxidizing acids such as nitric acid (HNO_3) and in so doing gives off nitrous vapor.

Silver is the eleventh element in the second long period; it has ten electrons in the penultimate level (4d) and one electron in the last level (5s). Its chemistry depends on this electronic configuration. Its normal valence state is +1, due to the loss of the 5s electron; in most of its compounds silver exists as the ion Ag^+. Under heavily oxidizing conditions,

GALVANIC SILVER-PLATING BATH—Silver is often used to coat less noble metals; this process is called silver-plating and can be carried out in a galvanic cell (Illustration 3a). The central bar is the cathode and the object to be plated is attached to it with copper plates, which ensure contact. Sheets of metallic silver act as the anode, and are hung from the two sides of the cell. A solution of a complex silver salt is used as the electrolyte. Illustration 3b shows a cupel furnace, a reverberatory furnace used to purify silver.

NATIVE SILVER AND ITS ORES—Native silver (Illustration 2a) is generally found in nature in the form of laminar or arborescent crystalline aggregates. When combined with other elements, it is found in argentite (Ag_2S), which forms large cubic crystals (Illustration 2b), and in pyrargyrite (2c) and proustite (2d), which are double sulfides with the formulas $AgSbS_3$ and $AgAsS_3$. In proustite the crystals are red in color and adamantine bright, explaining why miners often give the name of red silver to mixtures of the two ores.

compounds have been produced in which silver has valence states of +2 and +3, which involve the loss of one or two 4d electrons.

Because it is a transition element, silver can produce complex ions such as $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[AgCl_2]^-$, $[Ag(S_2O_3)_2]^{-3}$. These ions are colorless and easily soluble, and are often used to make the silver contained in insoluble salts complex.

Silver compounds include silver oxide (Ag_2O), which is obtained by treating solutions of silver salts with bases, and silver nitrate ($AgNO_3$), which is obtained by dissolving the metal in nitric acid. One of the few highly soluble silver salts, silver nitrate is used in a 1 percent solution as an eyewash and as a caustic agent when fused with a small amount of KNO_3; in the latter case it is sometimes called lunar caustic. Other compounds are silver nitride (Ag_3N) and silver fulminate (AgONC), both explosives.

All silver halides are sensitive to light: silver fluoride (AgF) is soluble and stable; silver chloride (AgCl), silver bromide (AgBr), and silver iodide (AgI) are insoluble and unstable to light. Silver chloride (AgCl) is white; silver bromide, yellowish; and silver iodide, yellow. Silver bromide is used in the manufacture of photographic emulsions.

The presence of silver in an ore or a solution (obtained by dissolving the ore) is detected by precipitating one of its salts and looking for the characteristic color—such as white in the case of silver chloride, black for silver sulfide, red for silver chromate, and yellow for silver phosphate.

PHOTOGRAPHIC PROCESSES

Film is manufactured by coating a transparent base, usually cellulose acetate, with gelatin containing silver bromide dispersed into very fine grains. When the film is exposed to light, the silver bromide goes through a process of reduction (or sensitization) to metallic silver. The reduction is proportional to the amount of light striking the various parts of the film. The reductive process, begun by the light, is completed by immersing the film in solutions containing reducing substances (ferrous sulfate or hydroquinone). This process, known as developing, is followed by fixing, which cleans the plate of the unreduced halide that would in time decompose and cause the whole plate to darken. Fixing consists of immersing the plate in a bath of sodium thiosulfate ($Na_2S_2O_3$), usually called "hypo." The thiosulfate ion dissolves the unreduced halide through the reaction $AgBr + 2(S_2O_3)^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + Br^-$. The result is a negative, an image in which the light areas of the object photographed are dark (because they are rich in metallic silver grains) and the dark areas, light. When light is passed through the negative and onto another emulsion, which is then developed and fixed, the dark and light areas are reversed. The result is a positive image—the finished photograph.

Films are being manufactured today that can be developed directly into positives without processing the film a second time. Such films are called reversible, and their positives are called transparencies.

CHROMIUM | the element that fights rust

Chromium, which is known primarily for its ability to prevent rust and corrosion, is also responsible for some of the most colorful compounds in chemistry. The element, number 24 in the periodic table, was discovered in 1797 by the French chemist N. L. Vauquelin and prepared in pure form the next year. Not until the twentieth century, however, was a method developed to produce chromium on an industrial scale.

This bright metal is a major component of meteorites, accounting for 0.03 percent of the Earth's crust. Its most important ore is chromite or chrome iron, $FeO \cdot Cr_2O_3$. Among the major producing areas are Republic of South Africa, Rhodesia, Cuba, and the Soviet Union. A less common but strikingly beautiful chrome ore is crocoite, $PbCrO_4$.

Chromium often replaces aluminum in its ores, although only in small amounts, because of the minute difference in radii of their respective trivalent ions. This difference, on the order of 0.10 Å, allows replacement of some aluminum ions by chromium ions without a change in the crystal structure. Emerald, for example, is an intense green variety of the mineral beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$), in which chromium replaces about 0.1 percent of the aluminum. Small as this percentage is, it is responsible for one of the world's most valued gems. The semiprecious aquamarine is a less brightly colored variety of the same mineral. Chromium impurities in aluminum oxide (corundum) account for the red ruby. Rubies can be produced synthetically, and are used to produce the intense red beam of certain lasers.

Both beryl and corundum are colorless; the beauty of the emerald and ruby is entirely due to chromium impurities. All chromium salts, in fact, are vibrantly colored, and the name of the element stems from *chroma*, the Greek word meaning color.

1a

CHROMITE AND CROCOITE—Chromite, $FeO \cdot Cr_2O_3$, is the most common ore of chromium. Large deposits of chromite (Illustration 1a) are mined in Republic of South Africa, Cuba, and the Soviet Union. Crocoite, a less common form, has brilliant red crystals, as shown in Illustration 1b.

OBTAINING CHROMIUM; ITS PROPERTIES AND ALLOYS

The first step in producing chromium is the removal of iron from chromite ore. The resulting chromic oxide, Cr_2O_3, can then be reduced with coal in an electric furnace:

$$Cr_2O_3 + 3C \rightarrow 2Cr + 3CO.$$

Another, more efficient method, employs aluminothermy, where the chromium obtained is 99.7 percent pure:

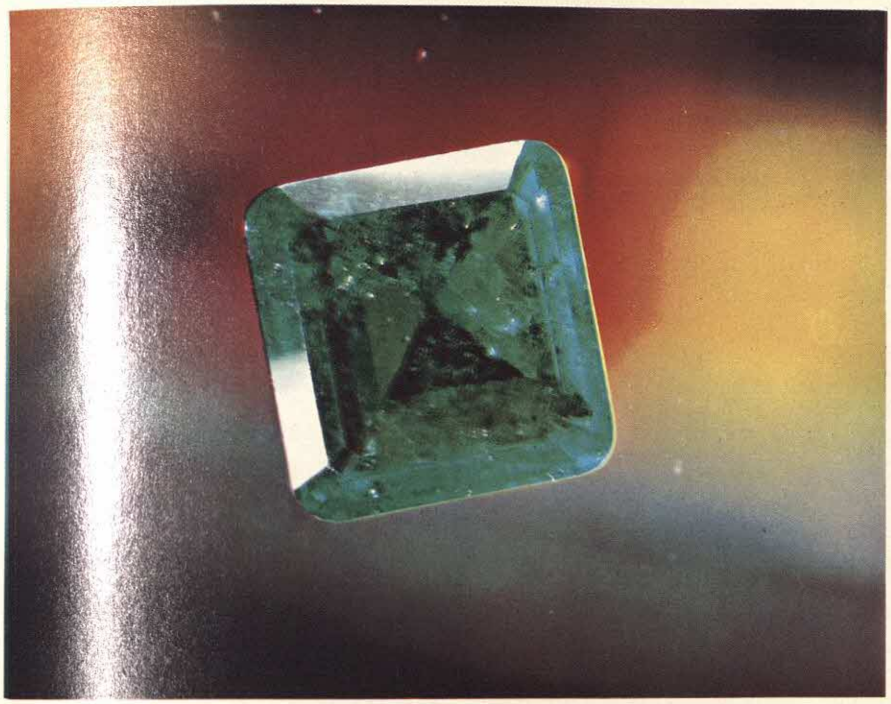
$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr.$$

Aluminum is a powerful reducing agent, and, when finely divided, burns vigorously to produce Al_2O_3 while liberating intense heat. Temperatures on the order of 2,000° C (about 3,630° F) can be reached, which aids the aluminum in reducing the oxide to the free metal. If the purity of the chromium is not critical, reduction of chromite with coal is sufficient. In this case, the resultant ferrous chromium alloy may be used directly in the production of special steels.

Chromium is a hard, gray, lustrous

1b

2a



2b

EMERALDS AND RUBIES—To a small degree, chromium can replace aluminum in its ores. Even though the amount of chromium is less than one percent in beryl, for example, the result is one of man's most prized gems: the emerald (Illustration 2a). The ruby in Illustration 2b is the result of chromium impurities in aluminum oxide.

metal. When it contains oxygen inclusions, however, it becomes brittle. While extremely resistant to attack from atmospheric agents, it is soluble in both hydrochloric and sulfuric acids. Interestingly, it is unaffected by either hot or cold nitric acid. Oxidizing acids, such as HNO_3, cause a layer of insoluble oxide to form on the metal's surface, making it impervious to further attack.

Chromium is probably best known as a plating material for other metals, both to decorate and protect. In the plating process, the object to be plated is attached to the negative pole (cathode) in a direct-current circuit, and placed in a bath of chromic oxide and an acid. Because chromium does not deposit in the absence of sulfates, sulfuric acid is used. When the electric current is turned on, the positive chromium ions in the solution migrate to the negatively charged electrode where they bond as a metal layer. The finest chromium plating is achieved if the object to be plated is first treated with nickel. The layer of chromium deposited is so thin that the electroplating process is used to plate precision equipment components without altering their dimensions to any appreciable degree.

In the steel industry, chromium plays a special role. It has the ability to impart strength and hardness to steels used for tools, engine parts, and ball bearings. Stainless and corrosion-resistant steels contain more than one percent chromium. Still other properties are manifested when chromium is used in combination with tungsten and nickel. Chrome-tungsten steels, for example, retain their hardness at temperatures in excess of 400° C (about 750° F). Such alloys find application in metal-working tools. Nickel-chromium steel, specifically a type known as 18-8 (18 percent Cr, 8 percent Ni), is a stainless variety favored in the chemical industry.

THE CHEMISTRY OF CHROMIUM

The characteristic oxidation states of chromium are +2, +3, and +6. In acid solution, these are equivalent to Cr^{2+} (chromous ion), Cr^{3+} (chromic ion), and $Cr_2O_7^{2-}$ (dichromate ion). In an alkaline environment, the ions are CrO_2^- (chromite) and CrO_4^{2-} (chromate), and the compound $Cr(OH)_2$ (chromous hydroxide).

The reduction of Cr^{3+} or $Cr_2O_7^{2-}$ with zinc yields the blue Cr^{2+} ion. Chromous salts are unstable in air, oxidizing rapidly to green chromic salts. This oxidation process may be observed in certain solutions where the change in color of the chromium ions from blue to green is vividly apparent. In contrast to chromous salts, chromic compounds in solution are stable, but slightly acidic due to hydrolysis of the chromic ion:

$$Cr^{3+} + H_2O \rightleftarrows CrOH^{2+} + H^+.$$

The chromic ion has amphoteric properties, reacting as an acid or a base depending on its environment. In acid solutions, its insoluble hydrate behaves like other metal hydroxides.

In the presence of bases, on the other hand, the reaction of the chromic ion is acidic. This behavior produces soluble acids in the form of the chromite ion, CrO_2^-. When a base is added to a trivalent chromium salt solution, a violet-colored gelatinous hydroxide is precipitated. The addition of more base dissolves the hydroxide, forming a dark green solution containing the chromite ion.

If the precipitated hydroxide is calcinated (heated at high temperature), green chromium oxide, Cr_2O_3, results. Known as chrome green, this compound is used as a paint pigment.

When dissolved in water, many chromic salts produce a deep violet color. The nitrate, chloride, and perchlorate are examples, forming a hydrate ion-complex with the water: $[Cr(H_2O)_6]^{3+}$. An equilibrium exists in the chlorinated forms between the violet and green states (in which two Cl atoms replace two water molecules in the complex):

$$\underset{\text{violet}}{[Cr(H_2O)_6]Cl_3} \rightleftarrows \underset{\text{green}}{[CrCl_2(H_2O)_4]Cl \cdot 2H_2O}.$$

A shift toward the green state occurs when either the temperature or concentration is increased. Trivalent chromium

ELECTROPLATING WITH CHROMIUM—Metals to be plated with rust and corrosion-resistant chromium are suspended in a bath of chrome salts. When electric current is applied, the positive chromium ions migrate to the negative pole, of which the material being plated is part.

3

CHROME ALUM—Because of its distinctive color, chrome alum is easily recognizable. It is one of the most common chromium compounds.

5

4

CHROMITE FORMATION—Treating the violet-colored solution of chrome alum in the flask at the left with dilute sodium hydroxide produces a gray-green precipitate of chromic hydroxide. The addition of more base dissolves the precipitate, forming the green chromite ion solution on the right. The green state occurs also from increased temperature.

6

A CHARACTERISTIC REACTION OF CHROMIUM—A chromate ion solution treated with sulfuric acid, hydrogen peroxide, and ether results in the deep blue color of the peroxy-anhydride, CrO_5, shown in the ether layer in the test tube.

7

FORMATION OF RED PERCHROMATES—Another reaction characteristic of chromium is the production of the perchromate ion when hydrogen peroxide is added to an alkaline chromate solution.

8

SODIUM DICHROMATE—Yellow sodium chromate reacts with sulfuric acid to yield the alkaline dichromate, an orange solution. Chromium produces a range of some of chemistry's most colorful compounds.

9

CHROMIC ACID—The dark solution in the beaker is a powerful oxidizing mixture capable of destroying organic materials. This chromic acid mixture is made from sulfuric acid (in the graduated cylinder) and potassium dichromate.

produces a variety of hexacoordinated complexes with ions or molecules containing "free" electron pairs, such as NH_3, CH^-, F^-, Cl^-, CHS^-, and H_2O. The general formula for these complexes is $(CrX_6)^{\pm n}$, and the extent of their charge is determined by the charge of the ions, which varies from -3 to $+3$. The chromium ion is located in the center of the octohedral structure of these complexes. The complexes also produce a spectrum of colors, ranging from violet and purple through green to yellow and orange.

Certain of the trivalent chromium salts have industrial importance. Sodium chromite ($NaCrO_2$), for example, is used as a mordant in dyeing. This salt is hydrolyzed in solution to form the insoluble hydroxide $Cr(OH)_3$, which is deposited on the fabric being dyed. It adheres to the fibers, fixing certain dyes (alizarin, for example) and forming very stable colored finishes.

$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ (chrome alum, whose crystals are a beautiful amethyst color) has the property of hardening leather and is used in the tanning industry. Because it is also used in the waterproofing and dyeing of fabrics, it is the most important of the soluble chromium salts.

In its highest oxidation state, +6, chromium usually forms chromates and dichromates. The chromate ion can be produced by oxidizing the chromite ion in the presence of an alkali and hydrogen peroxide (H_2O_2) or other oxidizing agent. The ion is tetrahedral in structure, with four oxygen atoms bound to a central chromium atom. A chromate solution is yellow in color, but acidification causes a change to orange due to formation of the dichromate ion:

$$2CrO_4^{2-} + 2H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O.$$

The reaction is reversed if a base is added. Both the chromates and dichromates are powerful oxidizers.

A dichromate solution acidified with concentrated sulfuric acid yields CrO_3. This compound, chromium trioxide, sometimes called chromic anhydride, crystallizes in red needle-like crystals. A mixture of CrO_3 and H_2SO_4 is used to clean glass laboratory apparatus because it oxidizes and destroys fats and other organic material.

Lead chromate, $PbCrO_4$, and basic lead chromate, $PbCrO_4 \cdot PbO$, are bright pigments, known respectively as chrome yellow and chrome red. They make excellent paint. Ammonium dichromate, $(NH_4)_2Cr_2O_7$, is an interesting compound. Its orange crystals are easily ignited, producing volumes of green ash (Cr_2O_3) in a quite striking volcanolike display.

In the presence of easily oxidized organic material, chromates and dichromates develop a sensitivity to light, and are reduced to trivalent salts. These salts have the ability to harden gelatin, and this property is the basis for a printing process known as phototypography. In this process, a metal plate is coated with fish glue and soaked in a potassium dichromate solution. Then, a negative of the material to be printed is placed on the dried plate, and both are exposed to strong light. The glue not exposed to the light can be washed off, while a positive of hardened glue appears in relief. When the plate is then etched with acid, the parts not protected by the glue are eaten away to some extent, resulting in a raised surface suitable for printing.

Because of the range of colored compounds produced by chromium, its salts and minerals are easily recognizable. On a quantitative basis, the formation of chromium hydroxide as a precipitate is the starting point for analysis of chromium content. The trained technician is able to determine with relative ease the amount of chromium in a substance.

NITROGEN | from the atmosphere to fertilizers and explosives

In 1772, when Daniel Rutherford was studying respiration and Joseph Priestley was burning materials in closed bell jars, both scientists noticed that two substances remained after the air's oxygen was exhausted. One of these was carbon dioxide, the other was inert gas that they called "mephitic air." Five years later the Swedish chemist C. W. Scheele determined that this gas constituted about 80 percent of the atmosphere. He also discovered its inability to support combustion and that it was unbreathable. Antoine Lavoisier, the father of modern chemistry, found the gas so inert that he called it azote, from the Greek word meaning lifeless. Because the element was present in nitrates, it was also known as nitrogen (meaning nitrate former); hence, its chemical symbol N.

1a

1b

1c

THE EFFECT OF LIQUID NITROGEN ON A GERANIUM—The effects on materials immersed in the supercold of liquid nitrogen are striking. Exposed to a temperature of −180° C (−292° F), a geranium is reduced to fragments.

Nitrogen occurs as the diatomic molecule N_2 in the atmosphere, of which it constitutes about 78 percent by volume. Combined with other elements, it is found in saltpeter (KNO_3) and in Chile saltpeter (primarily sodium nitrate, $NaNO_3$). Except for the sodium and potassium nitrates and ammonia (NH_3), nitrogen compounds rarely occur as minerals, mainly because of the high degree of solubility of nitrogen salts.

Despite the meaning of the word azote, nitrogen is an essential constituent of animal and plant organisms, and nitrogen compounds are found in amino acids—the building blocks of all proteins.

PREPARATION AND PROPERTIES

By exposing air to a readily oxidizable substance, all of the oxygen in the air will be used to form an oxide of that substance. For example, red-hot copper forms cupric oxide (CuO) in air, while yellow phosphorus burned in a closed atmosphere is converted to its pentoxide (P_2O_5). In either case, what remains of the air is primarily nitrogen. This is not pure nitrogen, however, but contains about 1 percent argon, about 0.04 percent carbon dioxide, and smaller quantities of the other noble gases. Pure nitrogen can be obtained by heating a solution of one of its salts. Ammonium nitrite treated in this way decomposes according to the reaction $NH_4NO_2 \rightarrow N_2 + 2H_2O$.

Nitrogen is a colorless, odorless, inert gas with a diatomic molecule, N_2. Under normal conditions, it combines with only the most active elements, such as lithium, calcium, and magnesium—and with the latter two only by heating. This chemical inertia results from the great stability of the bond within the molecule. In fact, production of nitrogen compounds poses considerable technical problems.

At standard temperature and atmospheric pressure, one l of nitrogen weighs 1.2025 g (about 0.04 oz). The critical temperature for nitrogen is −147.1° C (−232.6° F); above this point it cannot be liquefied no matter how much pressure is applied. The gas is almost insoluble in water, but like all gases becomes more soluble as the pressure increases. For divers and caisson workers, who must function at considerable pressures beneath the earth's surface, this pressure-solubility relationship is of primary concern. At great depths nitrogen is forced into the blood under pressure. If a diver ascends too rapidly, the gas forms bubbles in the bloodstream and prevents proper circulation. The result is the dreaded and deadly bends, or nitrogen narcosis.

INDUSTRIAL PRODUCTION

The fact that nitrogen has a lower boiling point than oxygen allows the production of nitrogen by fractional distillation of liquid air. Because these gases cannot be liquefied at normal temperatures, they must be cooled before compression to the liquid state. Nitrogen boils at −195.8° C (about −320° F), oxygen at −182.96° C (about −297° F); therefore, when the temperature of liquid air is raised from −200° C (−328° F), the first to vaporize is nitrogen.

The extreme cold encountered when air is liquefied has given birth to the science of cryogenics: the study of matter at low temperatures. The properties of matter are amazingly altered in this frigid environment. For instance, rubber completely loses its elasticity and becomes as fragile as glass; meat, eggs, and vegetables become as hard as iron and shatter when dropped; lead will ring as sweetly as the finest chimes.

Naturally, there are more practical aspects to cryogenics. Attempts to destroy typhus and diphtheria bacilli by immersion in liquid air have shown the remarkable strength of these organisms. Even after long exposure to supercold, they become viable when they are returned to room temperature. Surgical techniques using liquid nitrogen to freeze tissue have given excellent results, with wounds being free of infection and fast-healing. In the steel industry, special characteristics are imparted to metals by immersion in liquid nitrogen while they are still hot.

THE CHEMISTRY OF NITROGEN

Nitrogen is present in a large number of organic and inorganic compounds. Its most common valences are −3 and +5, a characteristic of the elements in Group

2a

2b

2c

2d

2e

NITROGENOUS FERTILIZERS—Fertilizers containing nitrogen compounds can be of animal origin (Illustration 2a), and are formed by the decomposition of animal wastes. More important commercially are chemical fertilizers such as ammonium sulfate $(NH_4)_2SO_4$ (shown in Illustration 2b), ammonium nitrate NH_4NO_3 (Illustration 2c), calcium nitrate $Ca(NO_3)_2$ (Illustration 2d), and urea (Illustration 2e).

V of the periodic table. Nitrogen compounds are known, however, in which nitrogen occurs in all oxidation states from −3 to +5.

With hydrogen, nitrogen forms a number of important compounds. Ammonia (NH_3), the most significant of these, is the starting point for the production of other nitrogen compounds. Direct synthesis of ammonia is a widely used method of combining atmospheric nitrogen. The reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$ is reversible and exothermic.

To be economic from an industrial standpoint, synthesis employs high pressure (about 1,000 atmospheres) and temperatures between 300° and 400° C (572° and 752° F). A catalyst, usually finely divided iron, is used to speed up the reaction. Ammonia can also be recovered as a by-product of coal distillation.

Ammonia is a gaseous, toxic compound that is lighter than air and has a distinctively strong odor. The gas is easily liquefied at normal temperatures. Because it absorbs great quantities of heat on evaporation, ammonia makes an excellent refrigerant. In an oxygen-rich atmosphere, it will burn and form explosive mixtures. Being highly water-soluble, it reacts easily with water to form ammonium hydroxide:

$$NH_3 + H_2O \rightleftarrows NH_4OH.$$

The base partially dissociates into ammonium (NH_4^+) and hydroxyl (OH^-) ions, and reacts with all acids to form their respective ammonium salts. Important ammonium compounds include ammonium sulfate, $(NH_4)_2SO_4$, and ammonium carbonate, $(NH_4)_2CO_3$, both used in fertilizers. Ammonium sufate can be found naturally in the volcanic areas of Tuscany, and the guano deposits in Peru are sources for naturally occurring ammonium carbonate. Aqueous solutions of ammonia are used in cleaning, dyeing, and paint manufacture. Elemental nitrogen or nitric oxide (NO) can be obtained by burning ammonia.

Other important hydrogenated nitrogen compounds include the rocket fuel hydrazine ($NH_2{-}NH_2$) and hydrazoic acid (HN_3). Certain heavy metal salts of this acid, $Pb(N_3)_2$ and AgN_3, for example, are explosive and are used as detonators.

Oxygenated nitrogen compounds include nitrous oxide (N_2O), produced by decomposing ammonium nitrate: $NH_4NO_3 \rightarrow N_2O + 2H_2O$, and an entire range of useful oxides. Nitrous oxide, commonly known as laughing gas, is colorless and odorless. It is anesthetic, especially combined with ethylene.

3

GUANO DEPOSITS—The only deposits of nitrogenous salts are found in Peru and Chile. They were formed originally by enormous accumulations of bird droppings that, in time, decomposed to primarily sodium and potassium nitrates.

Nitric oxide (NO) can be synthesized directly from the elements using an electric arc, or by reacting certain metals with nitric acid:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO.$$

Nitric oxide is colorless, but oxidizes rapidly in air to form nitrogen dioxide (NO_2), a red-brown, mildly poisonous, irritating gas.

A direct method for nitrogen dioxide production involves heating heavy metal nitrates:

$$2Pb(NO_3)_2 \rightarrow 2PbO + O_2 + 4NO_2.$$

At low temperatures, the NO_2 forms the tetroxide molecule, N_2O_4. Also called nitrous-nitric anhydride, the tetroxide in a water solution yields nitrous and nitric acids:

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3.$$

At room temperature, nitrogen trioxide, N_2O_3, is an unstable gas that decomposes according to the reaction $N_2O_3 \rightleftarrows NO + NO_2$.

Demonstrating nitrogen's +5 valence, nitrogen pentoxide, N_2O_5, is an oxygenated compound obtained by dehydrating nitric acid.

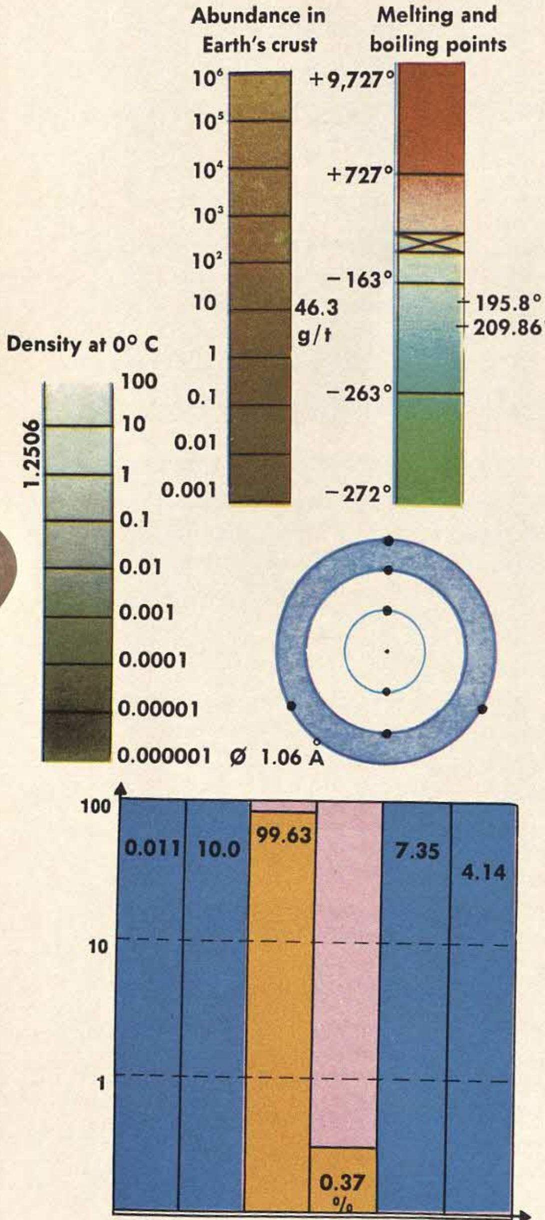
The two important oxygen acids of nitrogen—nitrous (HNO_2) and nitric (HNO_3)—are formed from the oxides in water. The first reacts to form valuable salts such as KNO_2 and $NaNO_2$. Nitric acid, however, has far greater commercial value, and is produced either from sodium nitrate:

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + HaHSO_4,$$

or by oxidizing ammonia. In its pure form it is a colorless liquid. Commercial aqueous solutions are often red, due to dissolved nitrogen dioxide. Commonly known as aquafortis ("strong water"), nitric acid is one of the most powerful acids and is a strong oxidizing agent.

In solution, nitric acid dissociates completely into hydrogen and nitrate ions. Through oxidation, it vigorously attacks many metals to form their nitrates and, in certain instances, reacts with reduction products such as NO_2, NO, N_2O, and ammonia. Some metals—such as chromium and aluminum—are not attacked by the acid because an impervious oxide forms on their surfaces. This explains why concentrated nitric acid can be transported in aluminum tankers. Organic substances, however, are not immune to attack. For example, turpentine ($C_{10}H_{16}$) treated with fuming nitric acid will ignite spontaneously. Finally, a mixture of three parts hydrochloric acid (HCl) to one part nitric acid, known as aqua regia, is the only solvent capable of dissolving gold.

4



DENSITY, ABUNDANCE IN THE EARTH'S CRUST, MELTING AND BOILING POINTS, ELECTRON CONFIGURATION, STABLE AND UNSTABLE ISOTOPES OF NITROGEN

5

ALUMINUM TANKERS AND STORAGE OF NITRIC ACID—Nitric acid is one of the most powerful oxidizing agents known. It readily attacks many metals, forming their corresponding nitrates. Some metals, among them aluminum and chromium, are resistant to this attack because of the formation of oxides on their surfaces. In the foreground, an aluminum tanker waits to transport its cargo of nitric acid.

Important fertilizers are the nitric acid salts of sodium and potassium. The powerful explosives TNT, nitroglycerin, and nitrocellulose are organic derivatives of the acid. While TNT is a relatively stable compound that requires a detonator to explode it, nitroglycerin is very unstable and sensitive to slightest shock. Nitroglycerin was first tamed by Alfred Nobel, who mixed the liquid with diatomaceous earth and invented dynamite. Cellulose nitrate (guncotton) forms gelatinous compounds and is mixed with other explosives.

Hydrocyanic acid, HCN (also known as prussic acid), is a highly poisonous nitrogen compound found in small quantities in bitter almonds. It can cause death in a matter of seconds. Antidotes for hydrogen cyanide poisoning include immediate oxygen inhalation and oral administration of ferrous hydroxide.

AGRICULTURAL USES OF NITROGEN

Large quantities of nitrogenous compounds are used in agriculture to maintain high levels of productivity. While nitrogen is a part of nature's biological cycle, this natural process is insufficient to keep pace with today's need for agricultural nitrogen.

Nitrogen's biological cycle is such that most plants cannot take this element directly from the atmosphere. Nor can they obtain it directly from ammonium compounds, which must be nitrified in the soil before they can be assimilated. Soil contains two types of bacteria that perform the function of nitrification. One oxidizes ammonia and ammonium salts to nitrites (the nitrosobacteria), and the other (nitrobacteria) oxidizes the nitrites to nitrates, which can be assimilated by plants. Only potatoes and certain plants that grow well in acid soils can use ammonium salts directly. Leguminous plants, such as peas and beans, can assimilate atmospheric nitrogen directly because colonies of bacteria thrive in the root nodules and transform the nitrogen into usable compounds.

The organic nitrogen in plants provides a source of animal nourishment. In the process of digestion, proteins are broken down by an animal into urea and uric acid, which are further decomposed in the soil to ammonia and elemental nitrogen, and the cycle continues. Today, artificial fertilizers are widely used to offset the tremendous amounts of nitrogen lost by land under heavy cultivation. Natural organic materials have declined to a minor place in supplying the nitrogen fertilizer of the world.

TECHNETIUM AND RHENIUM | the discovery and isolation of two rare elements

Although Mendeleev had forecast the existence and properties of technetium (Tc) in the development of his periodic table in the mid-nineteenth century, the element was not discovered until 1937. Technetium, atomic number 43, was discovered by two Italian physicists, C. Perrier and E. Segrè, who bombarded molybdenum with deuterons. The result was a radioactive material attributed to the decay of some newly formed element. The discoverers named the element from the Greek *technetos* (meaning artificial), to mark the creation of the first man-made element.

Recent attempts to isolate technetium from natural sources have focused on uranium ores because the element is formed as a fission product of some uranium isotopes, notably uranium-238. Success in these attempts, however, is measured in terms of about one one-millionth g of technetium from 5,000 g of pitchblende.

The isotopes of technetium that have been identified have mass numbers from 92 to 105. These isotopes are radioactive, decaying either by emission of an electron (beta particle) and changing into an isotope of ruthenium, or by absorbing an electron to become a molybdenum isotope. Technetium's isotopes include ^{101}Tc, with a half-life of 14 minutes; ^{95}Tc, with a 61-day half-life; and ^{98}Tc, with a half-life of approximately 1.5×10^6 years. (The term *half-life* refers to the time required for half the the atoms of an isotope to disintegrate. These half-life figures explain why technetium is not found in nature; any that might have been present at the Earth's creation would long since have decayed. Spectral studies of stars, however, indicate that technetium is present in some of them, though it has not been found in the sun.

ISOLATION OF TECHNETIUM

Technetium was first obtained in a measurable quantity by irradiating about 6,000 g of molybdenum with neutrons. Technetium was formed as a decay product of a molybdenum isotope, according to this reaction:

$$^{98}Mo + n \rightarrow {}^{99}Mo \rightarrow {}^{99}Tc + \beta$$

In the reaction, molybdenum-98 absorbs a neutron, n, to form an unstable isotope, ^{99}Mo, with half-life of 67 hours. In turn, ^{99}Mo decays to the ^{99}Tc isotope with the accompanying emission of a beta particle.

Following neutron bombardment, the molybdenum-technetium mass was dissolved in concentrated sulfuric acid and then distilled to collect technetium oxide, Tc_2O_7. The oxide was converted to the sulfide, and finally was dissolved in hydrogen peroxide to separate it from impurities and small quantities of rhenium.

This method works well, but only on a very small scale. Technetium is now isolated in practical quantities from nuclear reactors as a uranium fission product. About six percent of these products are technetium. The recovery process requires the storage of nuclear wastes for several years; this allows radiation levels to decrease, at which point the materials with the longer lives, such as technetium, can be safely obtained. Presently, several thousand g of the element are obtained annually by solvent extraction from other fission products and ion-exchange reaction for purification. The material is precipitated as the sulfide and finally reduced to the elementary state with hydrogen.

DISCOVERY AND ISOLATION OF RHENIUM

The existence of rhenium (Re) was also predicted by Mendeleev. The element was not obtained in any quantity, however, until 1925. Rhenium is one of the rarest of the nonradioactive elements. No ores of the element exist; its quantity in the Earth's crust is estimated to be on the order of 1×10^{-7} percent.

The discovery of rhenium is credited to the German scientists W. Noddack, I. Tacke, and O. Berg, who isolated it from manganese and tantalum ores in 1925. It is named from the Latin word for *Rhine* (*Rhenus*), because major sources of the metal ore were found in Mansfeld, Germany. Other concentrations of rhenium are found in copper sulfide ores mined in Arizona and Utah. Most rhenium is obtained from residual products from the working of these copper-bearing ores and molybdenite (MoS_2). The residuals are roasted in air, forming rhenium heptoxide (Re_2O_7) as one of the products in the fumes. The material is recovered, washed, and crystallized into potassium perrhenate ($KReO_4$). To obtain the metal, the perrhenate is reduced with hydrogen. While the element obtained in this manner may contain some potassium impurities, they pose no problems. Many rhenium isotopes are known, ranging from mass numbers 177 to 189. The only stable ones, however, are ^{185}Re and ^{187}Re. Because of the number of isotopes, the element is assigned an average atomic weight of 186.2.

Three years after its discovery and isolation, rhenium cost $10,000 per gram. By 1930, production had increased a thousandfold, bringing the price down to $3.00 per gram.

PROPERTIES OF TECHNETIUM AND RHENIUM

Both elements have hexagonal crystalline structures. Both have high melting points: that of technetium is about 2,200° C (about 3,990° F), while rhenium melts at 3,180° C (about 5,755° F), the next highest to tungsten, which has the highest melting point of all metals at 3,380° C (about 6,115° F), and to carbon, with a melting point of 3,550° C (about 6,420° F). The boiling point of technetium has not been determined; that of rhenium is estimated to be about 5,630° C (about 10,165° F).

Both metals are very reactive, oxidizing readily when heated in the powdered state. Halogens, with the exception of iodine, combine directly with both metals. Rhenium can be dissolved in hydrogen peroxide, and both metals are soluble in oxidizing acids (HNO_3 and hot H_2SO_4, for example), although they are insoluble in acids of the halogens such as HCl and HF.

The commercial form of rhenium is a black or grayish powder that can be

1a

1b

1c

RHENIUM COMPOUNDS—Some of the many colorful rhenium compounds are shown in Illustration 1a. These stable materials are formed by the element's +3, +4, +5, and +7 ions. Rhenium trioxide, ReO_3, is the reddish-brown compound in Illustration 1b; the lime-green compound in Illustration 1c is potassium hexachlororhenate, K_2ReCl_6.

converted directly into wire or sheet metal. It can also be produced in colloidal form, in which case it readily adsorbs hydrogen and can be used as a catalyst in ammonia production. Solutions of rhenium salts can be electrodeposited and, as such, are used to protect base metals from corrosion in a manner similar to chromium. Alloyed with tungsten, the metal is used for light-bulb filaments because of the high melting point of the resulting alloy. Because these alloys are subject to oxidation, however, they are enclosed in an atmosphere of inert gas.

Technetium, in the form of the pertechnate ion (TcO_4^-), has the ability to protect steels from corrosion, even in dilute concentration (5×10^{-4} percent). Interestingly, the ion concentration is critical, for beyond a certain point the corrosion inhibition properties disappear. It has not been fully established how this mechanism works, and there is no practical application for the process as yet. Technetium is always handled with caution due to its radioactive emission of harmful beta and x-rays.

In view of the extreme scarcity of both technetium and rhenium, both metals are recovered whenever possible.

THE CHEMISTRY OF TECHNETIUM AND RHENIUM

Until recently, technetium was ignored in favor of research into rhenium's chemistry. Today, though, chemistry is finding value in both metals. Both have similar chemical properties, though differing considerably from manganese, a lower homologue. For instance, manganese forms a stable Mn^{2+} ion, while +2 ions do not exist for technetium and rhenium.

Technetium forms stable Tc^{4+}, Tc^{6+}, and Tc^{7+}, while +3 and +5 states are difficult to obtain. While a rhenium ion in the +6 state cannot easily be produced, those ions with +3, +4, +5, and +7 valences produce stable compounds. Technetium and rhenium compounds are known in all oxidation states from −1 to +7. Both elements form a series of binary oxygen, sulfur, and halogen compounds. The oxides are very colorful, those of rhenium being black ($Re_2O_3 \cdot H_2O$), brown (ReO_2), red (ReO_3), blue (Re_2O_5), and yellow (Re_2O_7). Technetium's oxides are black (TcO_2), purple (TcO_3), and yellow (Tc_2O_7).

Rhenium sulfides catalyze the hydrogenation of organic material, and have the property of not being "poisoned" in the presence of sulfur compounds, as does platinum, another common catalyst. The elements also produce a considerable number of variously colored halides; some are stable, some not. The hexafluoride (ReF_6), pentachloride ($ReCl_5$), tribromide ($ReBr_3$), and two simple iodides (ReI_3 and ReI) have been reported. The trichloride ($ReCl_3$) is a trimeric red solid that behaves as a nonelectrolyte in solution; on heating, it emits a green vapor. From this vapor, metal may be deposited by thermal decomposition.

The acids of technetium and rhenium, $HTcO_4$ and $HReO_4$, are especially important in the formation of the respective pertechnate and perrhenate salts. The acids are stable oxidizing compounds, are soluble in certain organic solvents, and are easily absorbed by ion-exchange resins. These properties, in fact, are exploited in the extraction and purification of the metals. The pertechnates and perrhenates of tetraphenylarsine [$As(C_6H_5)_4^+$] are insoluble, and thus find use in gravimetric quantitative analysis of the elements.

SILICON | from mountains to window panes

Silicon, first used by the Romans to make glass, represents about 28 percent of the Earth's crust and is second only to oxygen in abundance. With the exception of the carbonates (limestones and dolomites), it is characteristic of all rocky matter. Silicon, which takes its name from the Latin *silex*, or flint, never occurs in the free state; it is found primarily as the oxide, silica (SiO_2), in sand, quartz, flint, opal, and a great many other minerals. Silicon's metallic oxide complexes include granite, asbestos, clay, mica, and many others.

QUARTZITE—Although it never occurs in a free state, silicon is the second most abundant element in the Earth's crust. It is found primarily in the form of silicon dioxide, or silica (SiO_2), of which quartz is the crystalline form and quartzite the compact rock variety.

1

In 1823, the Swedish chemist J. J. Berzelius succeeded in isolating the free element by heating sodium fluosilicate (Na_2SiF_6) with metallic sodium:

$$Na_2SiF_6 + 4Na \rightarrow 6NaF + Si.$$

Elementary silicon can now be prepared by several methods, and depending on the process is obtained in both crystalline and amorphous forms. X-ray studies of the amorphous form, however, have revealed a microcrystalline structure identical to silicon in the crystal state.

Silicon is a nonmetallic element resembling carbon in that it has several allotropic forms and in the number and variety of compounds produced. Its structure is similar to that of diamond; its crystals are lustrous and black. When heated in air, it burns brightly, forming the dioxide. At normal temperatures, silicon reacts vigorously with fluorine to produce SiF_4 (silicon tetrafluoride) but will combine with other elements only at high temperatures. In all but a very few instances silicon exhibits a +4 valence in its compounds, and, in fact, is a member of Group IVA in the periodic chart where tetravalence is characteristic.

Today, silicon is used in the steel industry in fabricating special alloys, and as an abrasive (silicon carbide), and is the foundation for the clay-working, glass, and cement industries. Of increasing importance is the manufacture of silicones—organic compounds in which part or all of the carbon is replaced by silicon.

OXYSILICON COMPOUNDS

The atoms of silicon are bound together by oxygen atoms to form chains. The structures resulting from this combination can be fibrous, layered, or three-dimensional. The only oxide of silicon found in nature is the dioxide, SiO_2. This compound crystallizes in various ways, however, to form a wide variety of minerals.

NEEDLE-LIKE CRYSTALS OF HORNBLENDE IN QUARTZ—The quartz crystal in the center of the illustration has inclusions of hornblende, seen as needle-like structures. Hornblende is an extremely complex mineral composed of an aluminum-calcium-iron-magnesium-silicon oxide combination.

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EPITAXY OF QUARTZ AND ORTHOCLASE—Epitaxy is an association of crystals that takes place according to well-defined natural laws. Illustrated is such an association between quartz and orthoclase, a common potassium feldspar.

Quartz is the major crystalline manifestation of silicon, and is found primarily in four geometric configurations: triangular, hexagonal, tridymite or rhombic, and cristobalite or tetragonal. Many varieties of quartz are vibrantly colored due to the presence of other elements as impurities; smoky quartz is brown, amethyst is purple, and onyx ranges from black to white. Jasper, a beautiful red, owes its color to traces of ferric oxide (Fe_2O_3). The iridescence of opal, a semiprecious stone, is due to small inclusions of a calcium carbonate. Opal and agate are varieties of amorphous silica.

USES OF SILICON DIOXIDE

If fused and cooled quickly, silicon dioxide (silica) becomes amorphous and vitreous. In this state, it is known as fused silica, and is used to make heat-resistant crucibles, flasks, and high-temperature thermometers. The coefficient of expansion for silica is so slight, in fact, that it resists breakage over ex-

treme temperature ranges. The thermometers mentioned above, for instance, can be heated to incandescence and plunged into liquid air without damage. Silicon dioxide is also resistant to stresses that would destroy other materials; it can be drawn into fine strands that are used in special applications. The glass, porcelain, and cement industries are the largest users of the compound.

A PRACTICAL USE FOR QUARTZ—This evaporating dish is made of fused quartz. When silica is melted and cooled quickly, the result is an amorphous, vitreous form. Quartz of this type—sometimes incorrectly called quartz glass—has a very low coefficient of expansion, making it suitable for utensils used in operations over a wide range of temperatures.

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OLIVINE—A silicon compound with the formula (Mg, Fe)$_2$SiO$_4$, olivine is a common mineral found in volcanic rock. Its characteristic color is due to the presence of bivalent iron. In the transparent green state, olivine is valued as a gem and is known as peridot.

SILICIC ACIDS AND SILICATES

Numerous silicic acids are produced by hydration of silicon dioxide. The more important varieties are:

1. Orthosilicic acid, H_4SiO_4, from which the following minerals are derived: topaz, $(AlF)_2SiO_4$, a colorless to yellow variety of quartz; olivine, $(Mg, Fe)_2SiO_4$, so called from its color, which is due to the presence of bivalent iron; almandite, $Al_2O_3 \cdot 3FeO \cdot 3SiO$, a variety of garnet; and muscovite, $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$, named for Moscow where once windows were made from this silicate.
2. Metasilicic acid, H_2SiO_3, from which beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$, is derived.
3. Metadisilicic acid, $H_6Si_2O_7$, which can be reduced to $Li_2O \cdot Al_2O_3 \cdot 8SiO_2$, a mineral petalite; other reduction products of this acid are serpentine, $3MgO \cdot 2SiO_2 \cdot 2H_2O$, and kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.
4. Metatrisilicic acid, $H_6Si_2O_7$, which produces the common orthoclase, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$.

Note that silicon is often replaced by aluminum, beryllium, and other elements. The first two produce commonly occurring aluminosilicates and berylsilicates.

Diatomaceous earth, formed from the skeletons of diatoms and radiolaria, is another silicon compound. This material has highly absorbent properties, and is so used as a filtering material. It is also employed in dynamite manufacture.

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ORTHOCLASE—This mineral, also known as potassium feldspar, is another very common compound, found primarily in igneous rock formations. Hydrothermal reactions may alter orthoclase, changing it to kaolin or other claylike materials.

AMPHIBOLITE—A very common mineral, amphibolite and its variations are constituents of metamorphic rock. Some forms of the mineral are variously colored and are used for decorative purposes.

CLASSIFYING SILICATES BY CRYSTAL STRUCTURE

Representing silicates by their chemical formulas gives no information as to physical properties. Hardness, for example, is reliant on structure; to determine structure scientists resort to x-ray crystallography.

The major, naturally occurring silicates can be classified by the arrangement of atoms in their crystal lattices. In the case of the feldspars, potassium, and sodium aluminosilicates, which account for about 50 percent of the Earth's crust, the structure is a three-dimensional cornice. In these compounds, the $(SiO_4)^{-4}$ group is often replaced by $(AlO_4)^{-5}$. Orthoclase, one of the feldspars, has four oxygen atoms located at the vertices of the silicate group tetrahedron, and each of these is matched by as many adjacent $(SiO_4)^{-4}$ tetrahedrons. This positioning results in a three-dimensional arrangement of the crystal.

Laminar silicates—those with stratified plane lattices—are structured so that each $(SiO_4)^{-4}$ tetrahedron is bonded to three more tetrahedrons by oxygen atoms. A fourth oxygen atom at right angles to the plane may, in turn, be bonded to a metal ion. This type of silicate includes the micas, which have a layered structure and can be peeled or cleaved along these planes, much like an onionskin. In silicates with chain or ribbon structures, each $(SiO_4)^{-4}$ tetrahedron is bound to another by two oxygen atoms. This configuration is repeated *ad infinitum*.

Finally, insular silicates, such as beryl, form crystals in which six $(SiO_4)^{-4}$ tetrahedrons are bound vertex-to-vertex.

The structure resulting from this bonding is a ring.

Thus, the degree of hardness is explained by the way in which the atoms in the crystal lattice of a silicate are bonded. More precisely, the way in which the $(SiO_4)^{-4}$ tetrahedrons are joined determines the crystal structure and its cleavability. The orthosilicates, for example, are relatively hard, owing to their three-dimensional structure. In contrast, the planar formation of talc gives it a soft quality.

OTHER SILICATE COMPOUNDS

Many silicon derivatives are assuming major industrial importance, especially the organic silicones. These complex compounds are oily, elastic, or resinous, and are widely used as lubricants and ingredients in rubber manufacture. The

JASPER—Silicon oxides, with traces of iron oxide, are usually homogeneous in color, ranging from red to green to gray. On occasion, formations with bands of color are found and used for decorative purposes in home and building interiors.

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silicones are highly resistant to heat and are chemically inert to metals. They are characterized by Si-C and Si-O-Si bonds. This important class of compounds is being increasingly used in a large number of areas, such as artificial organs.

Silicon carbide, SiC, is an exceptionally hard compound, exceeding the hardness of diamond. It is used as a grinding material and in tools for high speed drilling.

Silicon fluoride, when hydrated, forms hexafluosilicic acid, a compound found only in aqueous solution. Salts of this acid aid in preventing corrosion of certain porous, chalky materials. Silicon fluoride is also used as a disinfectant, an insecticide, and an opaquing agent in paint manufacture.

Without silicon, there would be no glass, ceramic, or cement industries. Glass, whose origin has been estimated about 5,000 years ago, is essentially a combination of silica, basic silicates, and alkaline-earth oxides. Since the composition of glass can vary, it is regarded as a solution even though its appearance and behavior is that of a solid. Glass has no well-defined melting point, and can be softened through a wide temperature range. This is physical proof of a noncrystalline structure.

Today's range of glass types is enormous, with a property and use for almost any purpose. From bottles to precision optical lenses, from unbreakable plate glass to safety glass for automobiles, for ornamental use or in cryogenics, a glass can be tailored to fill most any need.

Like glass manufacturing, the ceramics industry is very old. Products range from earthenware to porcelain to brick. Hydrated aluminum silicate—which is the basis for this industry—is known in the

POTASSIUM FELDSPAR—One of the characteristics of this mineral in its relatively pure state is long crystals. Normally colorless and transparent, though sometimes reddish, this feldspar is mixed with kaolin (another of its forms) to make ceramics and porcelains.

9

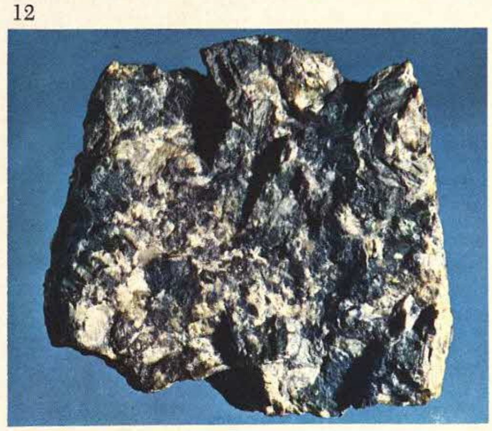
10

pure form as kaolinite; but when iron impurities are present it is clay. Both minerals possess considerable plasticity when mixed with water; when molded and fired—a process that dehydrates the material to form stable silicates—the mass becomes extremely hard. Fine porcelains are one result of this process; they contain no impurities and are translucent. In addition to its decorative use, porcelain is often used in laboratory and industrial processes and as an electrical insulator.

CROCIDOLITE—This mineral belongs to the family of amphiboles, or hornblendes. Also called blue asbestos, it is mined in South Africa in the form of fibrous aggregates. The sample in the illustration is a crocidolite amphibole on serpentine.

11

12



BRONZITE—This dark greenish-brown mineral is from the family of rhombic pyroxenes.

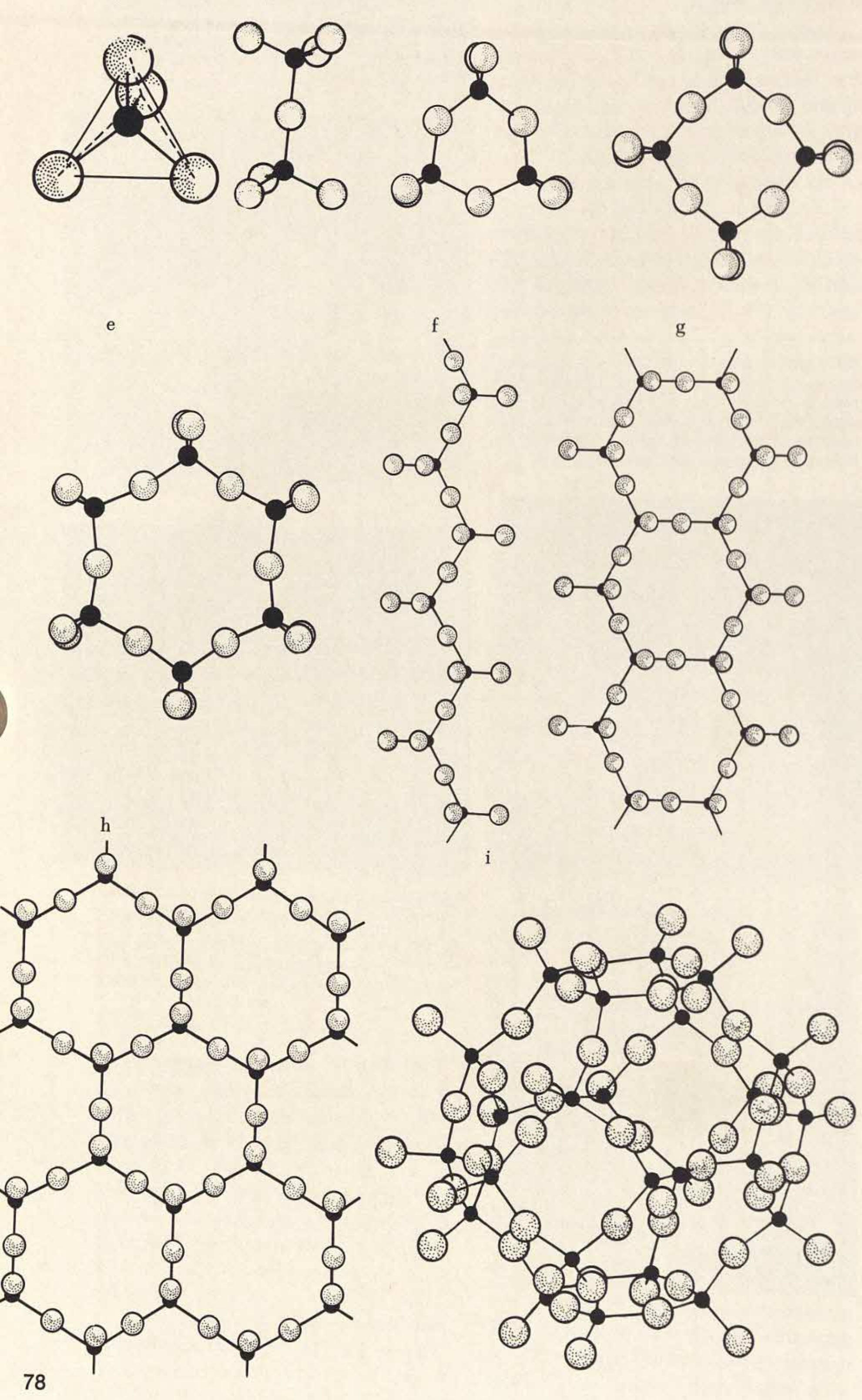
MUSCOVITE—This mineral belongs to the potassium micas. It is quite commonly found in sheets and can be peeled much like an onionskin.

Less highly prized is earthenware, commonly found in *objets d'art* and cooking utensils. Many kinds of brick and tile are manufactured by firing natural clay to which ferrous oxides have been added for color. Pure forms of clay are used to make refractory brick, a special material that is able to withstand high temperatures. Refractories are used to line furnaces in steel mills and for other high temperature operations.

One of the fundamental industries in the modern world is that of cement manufacture. Cement—which is actually a mixture of natural and man-made clay

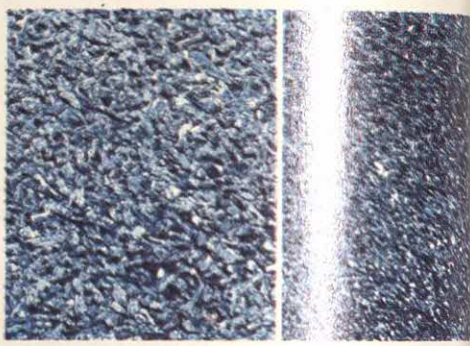
13

CLASSIFICATION OF SILICATES—Part **a** of the illustration shows the basic $(SiO_4)^{-4}$ tetrahedral structure. When the tetrahedrons are bonded in pairs through a vertex **b,** compounds such as hemimorphite or calamine are formed. The structures of cyclosilicates are shown in **c, d,** and **e,** of which beryl is an example. A simple chain of tetrahedrons as in the inosilicates, is shown in **f.** The pyroxenes are examples of these minerals. Characteristic of the amphiboles is the double chain **g,** while **h** represents the structure of the micas and claylike materials having a planar formation of the molecules. The complex representation **i** shows the three-dimensional group of tetrahedrons common to the feldspars (orthoclase).



14a

14b



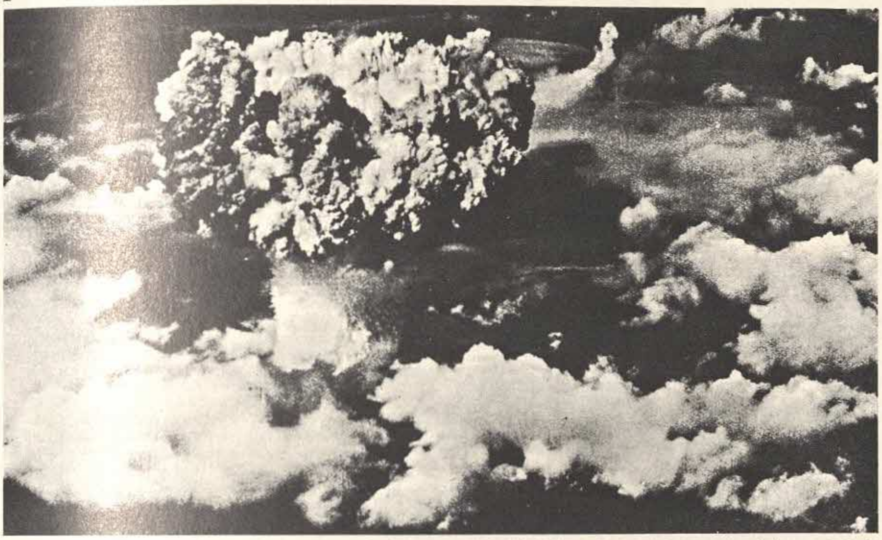
SILICONE GLASS AND SILICON CARBIDE—The ability of silicon to replace carbon in organic compounds results in the silicones—a series of materials finding increasing uses. Silicones are oily, resinous, or elastic substances used as lubricants and in rubber manufacture. Illustration 14a is a glass plate, part of which has been treated with a silicone. The water beads up on the treated part, while it spreads out on the untreated glass. The silicon carbide in Illustration 14b is used as a constituent of grinding tools and is harder than diamond.

and limestone—is formed by a process that begins with the firing of this mixture in rotary furnaces, or kilns, at temperatures of from 1,300 to 1,400° C (about 2,400 to 2,550° F). The partially fused material, or clinker, is removed from the kiln and allowed to cool before being ground to powder. Ordinary cement is called Portland, the name derived from a resemblance to a naturally occurring stone. Essentially powdered calcium aluminosilicate, its composition is 60 percent calcium oxide, 25 percent silica, and 5 to 10 percent aluminum oxide. It may also contain variable quantities of Fe_2O_3. In the firing process, all water is removed, resulting in the formation of stable silicates and aluminates. The addition of water to cement causes a complex setting mechanism to take place, involving a series of hydration and hydrolysis reactions.

Cement, like glass, is represented by various types, each with special characteristics. They differ with respect to setting speed, stress tolerance, and underwater durability.

URANIUM AND THE TRANSURANIUM ELEMENTS | the key to nuclear energy

1



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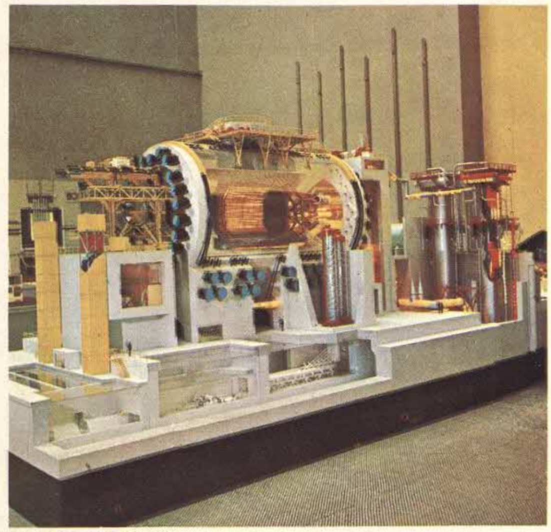


ATOMIC EXPLOSION — The characteristic mushroom-shaped radioactive cloud emits highly lethal radiation into the atmosphere. The atomic bomb consists of two masses of uranium-235 or plutonium. When the neutron shield holding these masses apart is ruptured, the quantity of fissionable material is able to exceed the critical mass, and an almost instantaneous high-energy explosion results.

ATOMIC REACTOR—An atomic reactor creates the possibility for controlled study of nuclear phenomena. The heart of an atomic reactor is shielded by thick layers of neutron- and radiation-absorbing material.

Working with pitchblende, the German chemist M. H. Klaproth recognized in 1789 the existence of an unknown element. Not until 1841, however, was the new element isolated by the French chemist E. M. Peligot, confirming the earlier prediction. The new element, a metal, was named uranium (U), for the planet Uranus. In 1872 Mendeleev predicted and then verified that uranium was the heaviest natural element. A few years later, the French physicist A. H. Becquerel made the important discovery that uranium was radioactive, thus laying the foundation for the systematic study of spontaneous nuclear transformation. In a sense, the dream of the alchemists had come true--one element could be changed into another. Only after the German physicists O. Hahn and F. Strassmann discovered the fissionable properties of uranium in 1939 did the metal become industrially important.

Yellow glass with a content of more than 1 percent uranium oxide, and dating back to A.D. 79, has been found near Naples, Italy. Thus, uranium has been used for centuries, although its properties remained a mystery for a similar time. In more recent times, uranium ores were used as a radium source for painting watch and instrument dials. Today, however, uranium is of vital importance to world commerce and politics. It has made possible the atomic bomb (an example of instantaneous fission) and the nuclear reactor (controlled fission). The latter has made cheap electric power a reality, in addition to providing a powerful research tool for the study of the progenitors of matter.

In atomic reactors, large numbers of neutrons are produced with a corresponding release of tremendous energy. Both the atomic bomb and nuclear reactors use the energy liberated by the nuclei of uranium-233 and uranium-235, and by plutonium isotopes of uranium-238. When one of these nuclei is struck by a neutron it splits into two lighter nuclei, simultaneously liberating two or three other neutrons and large amounts of energy. Graphically:

$$^{235}_{92}\mathrm{U} + \mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \xrightarrow{\text{fission}} {}^{139}_{56}\mathrm{Ba} + {}^{94}_{36}\mathrm{Kr} + 2.5\mathrm{n} + \mathrm{E}.$$

(The number to the lower left of each element is its atomic number, while the number to the upper left is its atomic weight. E is the energy released, in this case on the order of 200 Mev (million electron volts.)

The nuclei formed in this reaction are not always the same, nor are the neutrons produced or the energy liberated constant. The magnitude of the energy released is due to the fact that the sum of the masses of the reactants is greater than that of the fission products. The difference in masses has been converted to energy according to the relationships described by Einstein.

In fission reactions, each nucleus produces about 2.5 neutrons; these, in turn, cause similar reactions with other nuclei. The result is a chain reaction in which the entire mass is converted to fission products in a few seconds. This phenomenon does not occur in nature since uranium-235 (fissionable uranium) accounts for only 0.71 percent of natural uranium ore. In the case of pure uranium-235 in small amounts, liberated neutrons outnumber those able to cause further decay. However, when the weight of the material reaches a critical mass, the relation of neutrons to nuclei becomes unstable. Assuming each nucleus can liberate two neutrons, each of these can collide with two more nuclei. This process, taking place in a matter of seconds, continues geometrically until the entire mass fissions to cause an atomic explosion. This is the basis for the atomic bomb, in which two quantities of fissionable material, each of less than critical mass, are held apart by a neutron shield. When these two quantities are brought together, the

critical mass is exceeded to produce a nuclear reaction as described.

The explosion of an atomic device is termed an uncontrolled reaction. In nuclear reactors, however, the number of neutrons versus the fissionable material is held in check, or controlled. The heart of a nuclear reactor consists of its "fuel"—uranium bars. The uranium may be either elemental, an oxide, or an alloy of the oxide. Alloys are used to improve the mechanical characteristics of the bars, since they are required to withstand high temperatures. In any case, the nuclear fuel is surrounded by a moderator (such as graphite, heavy water, beryllium oxide, or silicon carbide) that reduces the speed of the neutrons. Uranium-235 is made to fission more easily with "slow" neutrons, while uranium-238, after being transformed into plutonium, fissions only with high-energy neutrons.

To control the neutrons and prevent explosions, materials such as cadmium that absorb neutrons are interspersed among the fissionable matter in reactors. Depending on the amount of neutron-absorbing material exposed to the neutron source, the reaction can be hastened or slowed as required. In order to protect the areas around the reactor from damaging radiation, thick shields of lead, concrete, graphite, or other substance surround the reactor. For a high-power reactor without any shielding, personnel would have to remain at least five miles
3 away to be safe from radiation.

ORES AND PROCESSING

The principal source of uranium is pitchblende, a uranium oxide of variable composition, whose general formula is $(UO_2)_x(UO_3)_y$. Deposits of industrial importance are widespread, occurring in the Democratic Republic of the Congo, Canada, the United States, Czechoslovakia, Portugal, and elsewhere. Secondary sources are chiefly the phosphates, arsenates, and vanadates, which contain other metals in addition to uranium. Among these ores are: brannerite, $(U, Ca, Fe, Th, Y)_3Ti_5O_{16}$, found in the United States and Canada; davidite $(Fe, Ce, U)(Ti, Fe, V, Cr)_3(O, OH_7)$, found in Australia; autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 10\text{-}12H_2O$, and carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 8H_2O$, both found in the United States; and tynyamunite, $Ca(UO_2)_2(VO_4)_2 \cdot nH_2O$, found in Siberia.

Presently, only the richer uranium deposits are mined, with the less productive sites being held in reserve for future needs. The estimated reserve of uranium is well into the millions of tons. This represents a substantial energy source, since one pound of ^{235}U has greater potential heat energy than 1,000 tons of coal.

Uranium is extracted from its crushed ores by digestion in strong acids or alkalis, the choice depending on the oxidation state of the metal and the nature of the ore. Acid solutions produce the uranyl ion, UO_2^{2+}, or the metallic U^{3+} and U^{4+} ions. The alkaline process employs sodium or ammonium carbonates and bicarbonates to form salts of the uranyl carbonate complex $[UO_2(CO_3)_3]^{4-}$. The uranium is precipitated as the xU_2O_7 compound by ion exchange or solvent extraction. It is further purified to the UO_3 oxide, and then reduced with hydrogen to UO_2, which can be used as nuclear fuel.

When treated with hydrofluoric acid, the UO_2 produces UF_4, which can be fluoridated further to UF_6. The former compound can be reduced to elementary uranium with calcium or magnesium. UF_6 is used to enrich ^{235}U.

PHYSICAL AND CHEMICAL PROPERTIES

One of the most dense of the metals, uranium exists in the solid state in three crystalline forms. Normally found as the orthorhombic alpha form, it changes at 663° C (about 1,225° F) to a tetragonal or beta form. In turn, at 765° C (about 1,405° F) it is converted to the gamma or cubic structure, having a melting point of 1,132° C (about 2,070° F).

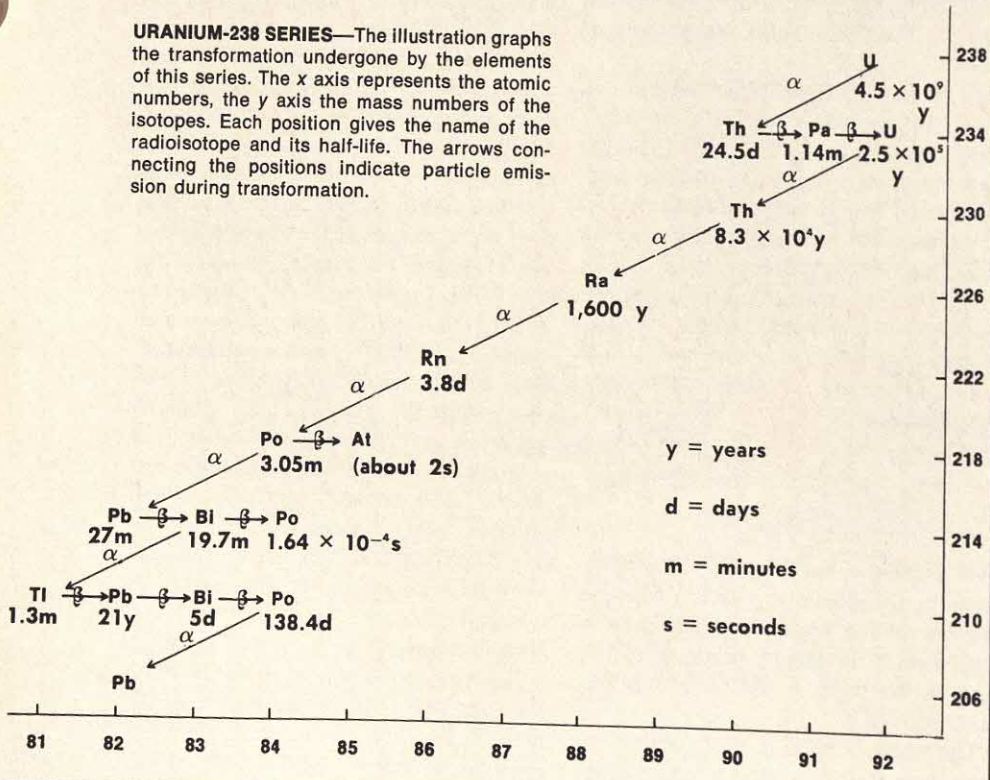
Uranium's natural isotopic composition is 99.27 percent ^{238}U, 0.72 percent ^{235}U, and 0.006 percent ^{234}U. Another important isotope, ^{233}U, is obtained from thorium by nuclear reaction. Its primary use is as a reactor fuel. Illustration 3 is a transformation chart of uranium-238. It is a very reactive metal, especially when finely powdered, in which case it reacts with water and is pyrophoric. At elevated temperatures it forms azides with nitrogen and carbides with carbon.

Uranium has a complex chemistry that has been the subject of much research. Among its known compounds are uranium hydride (formed directly from the elements, and very reactive), and several oxides, of which the most important are UO_2, UO_3, and U_3O_8.

With lithium, uranates of the $Li_2U_2O_7$, Li_2UO_4, and Li_4UO_5 type are formed. Uranium readily forms compounds with the halides, of which the fluorides are examples: UF_3, UF_4, UF_5, and UF_6. It also forms many binary compounds with elements like B, C, N, P, S, As, Se, Si, and Te. Uranyl salts UO_2^{2+} are also quite common, the most important being uranyl nitrate. This is soluble in many organic solvents, a fact used to extract the nitrate from aqueous solutions.

THE TRANSURANIUM ELEMENTS

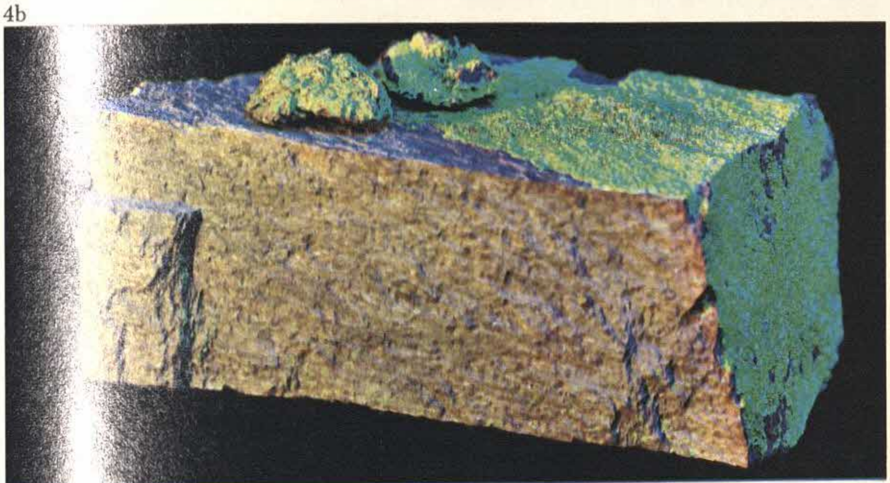
Because the half-lives of the more stable isotopes of the transuranium elements are so short, primordial quantities of these



URANIUM-238 SERIES—The illustration graphs the transformation undergone by the elements of this series. The x axis represents the atomic numbers, the y axis the mass numbers of the isotopes. Each position gives the name of the radioisotope and its half-life. The arrows connecting the positions indicate particle emission during transformation.

4a

4b



4c

4d

4e

URANIUM ORES—Illustrations 4a and 4b are samples of autunite, a calcium uranyl phosphate. The former shows the mineral in natural light, while the latter shows the fluorescence of the mineral under ultraviolet light. Pitchblende, also called uraninite, is the mineral in Illustration 4c. Illustration 4d is uranocircite, a complex mineral of composition $Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$. Finally, Illustration 4e is an example of torbernite, a copper uranyl phosphate often associated with autunite.

elements should have long ago disappeared. However, traces of neptunium and plutonium have been isolated in uranium ores where they form according to the reactions:

$$^{238}U + n \rightarrow {}^{239}U + \gamma \rightarrow$$
$$^{239}Np + \beta \rightarrow {}^{239}Pu + \beta.$$

These reactions have industrial application in the production of appreciable quantities of neptunium and plutonium.

The discovery that the transuranium elements could be obtained in this way is of considerable historical interest. In 1934, a team of physicists headed by Enrico Fermi found that a considerable number of radioactive substances could be obtained by the irradiation of uranium with neutrons. It was also discovered that some of the matter produced in this way did not possess any of the chemical properties of any known element. The existence of the transuranium elements was thus postulated. Later research proved this hypothesis to be correct. Then, when Strassmann and Hahn studied the products of the irradiation reaction, it was learned that the formation of "medium heavy" elements in these products was due to uranium fission.

Only plutonium is more than a laboratory curiosity, however, since neutrons cause a fission reaction enabling the use of polonium as a reactor fuel and in the production of atomic devices. The elements following plutonium are obtained in reactors capable of producing very intense neutron streams. Traces of the elements above number 96 can be obtained by bombarding plutonium, americium, and curium with the accelerated ions of boron, carbon, nitrogen, neon, or oxygen.

It is only with difficulty that the physical and chemical properties of these elements can be studied since they are formed along with highly radioactive fission products. Special equipment for handling by remote control, and methods for working with infinitesimal amounts had to be developed. In addition to the radiation hazard, plutonium is highly toxic, a dose of 10^{-6} grams being fatal. Americium, neptunium, and plutonium can be separated by taking advantage of the fact that their compounds exhibit varying degrees of solubility and volatility. They can be obtained in the metallic state by reduction of their fluorides with lithium or barium at 1,200° C (2,192° F). Neptunium's melting point is about 640° C (1,184° F), and plutonium goes through at least six phase changes before melting at 639.5° C (about 1,182° F). In each of the phases, the density, coefficient of expansion, and hardness are different. All three elements form oxides, some having the same structures as the uranium oxides with which they are isomorphic. Their halides also correspond to uranyl halides. Beyond americium in the periodic table, little is known about the elements.

SODIUM | a long known and vitally important element

Sodium compounds have been used by man for centuries, and are perhaps the oldest known materials. Sodium carbonate is referred to in ancient texts, and over 2,000 years ago this compound was studied by the chemists of the time. The ancient Hebrews discovered the antiseptic properties of sodium carbonate, using it as a dressing for wounds and to "cure" fevers. They called it *neter* from the Hebrew for "effervescent."

Later, the Greeks adopted the use of sodium carbonate, calling it *natrium*, a term also used for sodium nitrate. Subsequently, the two salts were differentiated; the word natrium was kept for the nitrate, while the word natron was given to the carbonate. It is from the latter that the alchemists derived the symbol for the element: Na.

The Arabs also discovered uses for sodium carbonate, producing soap and glass from the marine "kali" plants that are rich in this salt. The name "kali" became the root for the term "alkali metals," the group of elements containing sodium, potassium, lithium, rubidium, and cesium.

During the Middle Ages, sodium carbonate was called "soda" from the Latin *solida*. From the salt, the name was passed to the element; hence, sodium.

In 1790, the English chemist Sir Humphry Davy first obtained metallic sodium by heating the oxide Na_2O with carbon. Then, in 1807, he produced the element by the electrolysis of molten sodium hydroxide.

1

SALT PANS—Because of its great reactivity, sodium is never found naturally in the free state. However, it is very abundant and widespread in combination with other elements. As sodium chloride, it is found in the oceans and in some inland lakes. The illustration shows such a salt deposit.

2

ROCK SALT—Ancient seas, long since evaporated, deposited layers of rock salt. The crystals of rock salt in the illustration are colored by metallic impurities.

While it forms numerous compounds, sodium is never found in the free state because of its vigorous reactivity. Its best-known compound, sodium chloride, is found in large quantities in the oceans and in some inland lakes. For example, the Great Salt Lake in Utah contains so much salt that the lake's buoyancy is considerably greater than that of fresh water. Commercially important rock salt deposits are the result of the evaporation of ancient lakes and seas.

Of the salts found in the oceans, 30 percent are sodium salts. Nitrate deposits on the coast of Chile and carbonate deposits in Asia and Africa are plentiful sources of important compounds.

The more important sodium minerals include cryolite, a sodium-aluminum fluoride of which rich sources exist in Greenland; borax (sodium tetraborate); and the sulfate (Na_2SO_4).

Physiologically, sodium chloride is vital, for it maintains the proper electrolyte balance within the human body.

PREPARATION OF METALLIC SODIUM

Industrially, preparation of elemental sodium is not too far removed from Davy's method: electrolysis of the molten hydroxide. A similar method involves the fused chloride.

Hydroxide electrolysis is the primary method of preparation. In order to lower the compound's melting point, sodium fluoride and calcium chloride are added to the hydroxide. With this mixture, melting occurs at about 600° C (1,112° F) and the molten mass is electrolyzed with a graphite anode and an iron cathode. Because the molten sodium floats on the fused mass, it is easily separated. Extremely pure sodium can be obtained by distillation of the metal in a vacuum.

CHEMICAL AND PHYSICAL PROPERTIES

Sodium is a silvery metal, but because of its rapid oxidation in air it is rarely seen as such. Because of this reactivity, the metal must be stored away from contact with air—under oil, for example. At elevated temperatures, sodium gives off a violet vapor, and it burns with an intense yellow flame.

On contact with water, metallic sodium reacts with extreme rapidity, decomposing the water to form sodium hydroxide and hydrogen: $2Na + 2H_2O \rightarrow 2NaOH + H_2$. It also reacts strongly with alcohol, yielding a sodium alcoholate and hydrogen:

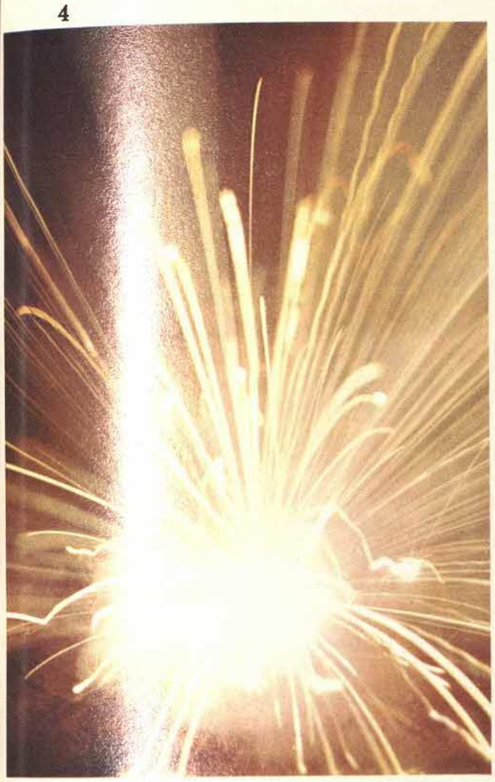
$$2Na + 2ROH \rightarrow 2RONa + H_2.$$

In all its reactions, sodium exhibits a +1 valence, a characteristic of the Group IA elements. Metallic sodium is widely used as a reducing agent, and is so effective that it is often amalgamated with

3

METALLIC SODIUM—Metallic sodium is stored under oil because it oxidizes rapidly in dry air and forms the hydroxide in moist air. At room temperatures, the metal is soft enough to cut with a knife.

4



AN EXPLOSION OF SODIUM—When ignited, metallic sodium burns explosively and gives off a strong yellow light.

mercury to reduce the vigor of the reaction. Many organic syntheses make use of this amalgam.

SODIUM PEROXIDE

This powerful oxidizer, Na_2O_2 is prepared by heating sodium in a stream of oxygen. One of the uses of this compound is in the manufacture of hydrogen peroxide, while its oxidizing properties make it suitable for use in bleaching textiles. Since sodium peroxide absorbs carbon dioxide, it is also used to purify air; one of the products of the purification reaction is oxygen:

$$2Na_2O_2 + 2CO_2 \rightarrow 2Na_2CO_3 + O_2.$$

SODIUM HYDROXIDE (CAUSTIC SODA)

From an industrial standpoint, sodium hydroxide, NaOH, is a very important compound. It is prepared either by the electrolysis of sodium chloride solution or by treating sodium carbonate with calcium hydroxide.

The electrolysis reaction requires a mercury cathode on which the sodium is deposited as an amalgam. This is then decomposed in pure water. The result is pure sodium hydroxide at a concentration of about 60 percent:

$$NaHg_4 + nHg + H_2O \rightarrow H_2 + NaOH + (n+4)Hg.$$

The reaction between sodium carbonate and calcium chloride is one of simple substitution, although the sodium hydroxide obtained is considerably less pure:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3.$$

The calcium carbonate, being less soluble, is precipitated, and the caustic soda solution filtered.

Sodium hydroxide is a white, fibrous-looking, translucent solid; in an impure form it is known as household lye. It readily absorbs water from the air, becoming a caustic liquid. The compound dissolves easily in water, giving off considerable heat, and solutions of sodium hydroxide readily attack glass, although metals such as silver, nickel, and iron resist its corrosive nature. Severe burns can result after contact with human skin, and sodium hydroxide should be considered at least as hazardous as sulfuric acid.

In addition to its use in analytical chemistry, sodium hydroxide is used in large quantities in soap manufacture and in the making of paper, textiles, and dyes.

SODIUM CHLORIDE

Sodium chloride, NaCl, is common table salt, the best known and most widely used of the sodium compounds. When found as rock salt deposits, it is mined in the same way that other minerals are obtained, and can be used directly as the pure compound.

Depending on the climate, the extraction of salt from seawater is carried out in different ways. In cold countries, the salt-laden water is allowed to freeze in large pans. Since fresh water freezes at a higher temperature than salt water, the ice that forms is removed. The remaining solution is allowed to freeze again, further concentrating the salt. Finally, the concentrated solution is evaporated in special boilers.

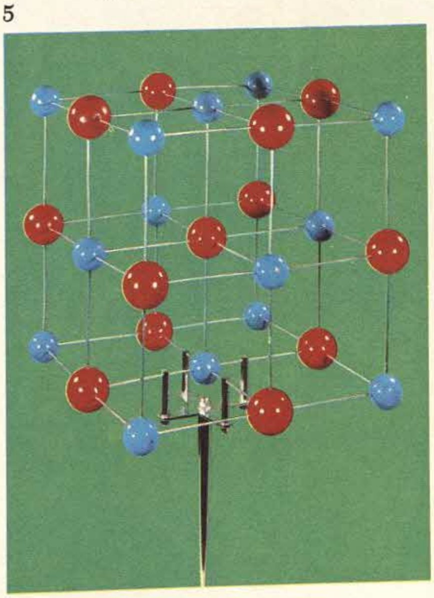
In warmer climates, the seawater is allowed to evaporate from pans or reservoirs exposed to the sun's heat. As the water evaporates, the salt concentration becomes greater, and the liquid is placed in other basins where less soluble salts are deposited. Since sodium chloride is very soluble in water, it is the last to be deposited, and the result is a very pure substance.

The solubility of sodium chloride is about the same in either hot or cold water. Therefore, it can be crystallized only by concentration. Sodium chloride crystals are members of the cubic crystal system. Though generally clear to translucent, they may be tinged with color due to the presence of metallic impurities.

Almost any sodium compound can be prepared from the chloride. Salt is, therefore, one of industry's most essential raw materials. It is also one of the basic ingredients in human nutrition and is used as a preservative for food and skins, to make soap, in glass manufacture, and in a host of other materials. It is also used in the glaze and enamel trades.

CRYSTAL STRUCTURE OF SODIUM CHLORIDE—This structural model shows the octahedral arrangement of the sodium and chlorine ions in a crystal of sodium chloride.

5



6

CRYSTALS OF TABLE SALT (SODIUM CHLORIDE)—Sodium chloride is of fundamental dietary importance. It is also used as a preservative of foodstuffs and as the starting point for the preparation of many sodium compounds.

7

a

b

TABLE SALT AND THENARDITE—Table salt is nothing more than sodium chloride, NaCl, commonly seen as small crystals as in Illustration 7a. The sodium mineral thenardite seen in Illustration 7b is anhydrous sodium sulfate, Na_2SO_4. This mineral can be found in the form of bipyramidal crystals.

SODIUM SULFATE

This compound, Na_2SO_4, is found in large deposits in Spain, Siberia, and Italy. In the laboratory the compound is easily prepared by an exchange reaction between two salts such as magnesium sulfate and sodium chloride:

$$MgSO_4 + 2NaCl \rightarrow Na_2SO_4 + MgCl_2.$$

Sodium sulfate has medicinal uses as well as use as a raw material in the glass and dye industries.

SODIUM SULFITE AND SODIUM BISULFITE

Sodium sulfite, Na_2SO_3, is a weak bleach for wool and silk and is used in photography to dissolve silver salts. The bisulfite, $NaHSO_3$, is used in making dyes, in tanning, and as a preservative for wine. Sometimes this compound is added to meat to improve its color.

SODIUM CARBONATE

Of all the alkali metal salts, sodium carbonate, Na_2CO_3, is undoubtedly the most important industrially. The compound is contained in certain marine plants and in some rocks as a mineral. Deposits are found in Africa and Asia where the carbonate is often accompanied by the bicarbonate in the double salt: $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$.

While sodium carbonate used to be produced on an industrial scale by the LeBlanc process, the cheaper and simpler Solvay process now produces all industrial carbonate. In this process, a saturated solution of sodium chloride is first treated with ammonia and then with carbon dioxide:

$$NaCl + NH_4HCO_3 \rightarrow NH_4Cl + NaHCO_3.$$

The products of this reaction are then heated to yield sodium carbonate, carbon dioxide, and water:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O.$$

The liberated carbon dioxide is further treated to yield ammonium bicarbonate.

Solvay soda, as sodium carbonate produced in this way is called, is used to make a wide range of goods, among them soap and glass.

Another well-known sodium salt is the bicarbonate, the cook's baking soda. When extremely pure, sodium bicarbonate is used medicinally to neutralize excessive stomach acidity, reacting as a weak base with the stomach's hydrochloric acid:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

Externally, a paste made of water and sodium bicarbonate is used as a first-aid treatment for minor burns. Because of the ability of the carbonate ion to precipitate calcium and magnesium ions, sodium bicarbonate is often used as a water softener.

Sodium carbonates form the constituents of many mineral waters and occur as the principal saline components in natron lakes, as efflorescences in Lower Egypt, Iran, and China, and as trona in Mexico, Colombia, and Venezuela. Enormous deposits of carbonates, mixed in some cases with sulfate and with chloride, occur in California, Nevada, and Wyoming.

SODIUM THIOSULFATE—One of the unique properties of this compound is its ability to make a "freezing" mixture through supersaturation. If 20 g of the salt are dissolved in 20 ml of water, the solution becomes cold, and agitation causes crystals of the thiosulfate, $Na_2S_2O_3$, to form.

8

ARSENIC | medicine and malevolence

In his book *De Arsenico,* the Swedish chemist T. O. Bergman noted in 1777 the probability that arsenic was the first element to be discovered by the roasting or smelting of its ores. When these ores are heated, dense fumes with strong, garliclike odors are given off. Long before Bergman, however, the Greeks were familiar with arsenic ores. Aristotle's *Mechanical Problems* mentions arsenic sulfide, which he called orpiment. Both Theophrastus and Dioscorides also recognized the existence of arsenic compounds. The Greek word *arsenikon,* from which the name derives, means "masculine" (and, indirectly, "virile or strong") —from the belief that metals were of different sexes.

The ancients always confused the element with its compounds, however, and it was not until the thirteenth century that the German scholar and scientist Albertus Magnus obtained the free element by heating arsenous sulfide with soap. In 1817, the Swedish chemist J. J. Berzelius studied the reactions of arsenic with various elements.

ORES AND PROCESSING METHODS

Though not abundant, arsenic is widely distributed in nature. Traces can be found in organic matter, and often in ordinary tap water. Rarely found in the native state, arsenic generally exists as an arsenide and a sulfarsenide. Almost all metallic sulfides contain a certain amount of arsenic. Many of the pyrites (FeS_2), for example, which are used in the production of sulfuric acid, contain arsenic impurities.

Arsenic's most important ores are orpiment (As_2S_3), realgar (As_2S_2), and arsenopyrite ($FeAsS$). Commercial deposits are found in California, Mexico, Canada, England, and East Germany. The trioxide (As_2O_3), called arsenolite, has a garliclike odor and is formed by the action of the atmosphere on other arsenic ores. In certain instances arsenolite is oxidized to soluble arsenates, thus finding its way into water supplies.

The element is obtained in a number of ways, one of which is the heating of arsenopyrite in the absence of air. In this process, the arsenic sublimes and is collected on the relatively cool walls of the roasting ovens while iron sulfide remains as "clinker":

$$4FeAsS \rightarrow 4FeS + As_4.$$

The same ore, roasted in the presence of air, also produces the element, but as an intermediate to be further reduced:

$$4FeAsS + 10O_2 \rightarrow 2Fe_2O_3 + 4SO_2 + As_4O_6.$$

The ferric oxide remains in the ash, the sulfur dioxide escapes as a gas, and the arsenic trioxide sublimes on the walls of the ovens. To form the element, the trioxide is then collected and reduced with carbon:

$$As_4O_6 + 6C \rightarrow 6CO + As_4.$$

Most industrial arsenic is produced in the United States and Sweden. Long used as a rodenticide and insecticide, arsenic is now finding increasing use in the electronics industry as a "doping agent" in transistors and other semiconductor devices. Recently, an alloy of the metal with gallium has been used to produce low-cost lasers capable of converting electricity into coherent light.

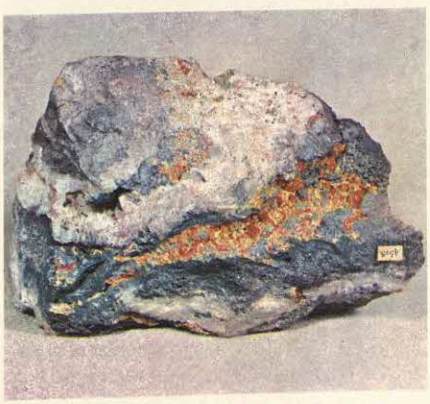
Because arsenic is a higher homolog of phosphorus, arsenic remembles it both chemically and physically. Like phosphorus, it has several allotropic elementary forms. Yellow arsenic has a cubic structure and is as soft as wax. This form is obtained by cooling the white fumes of arsenic vapor with liquid air; the product is unstable.

Gray arsenic is orthorhombic in structure, is stable at room temperatures, and

1

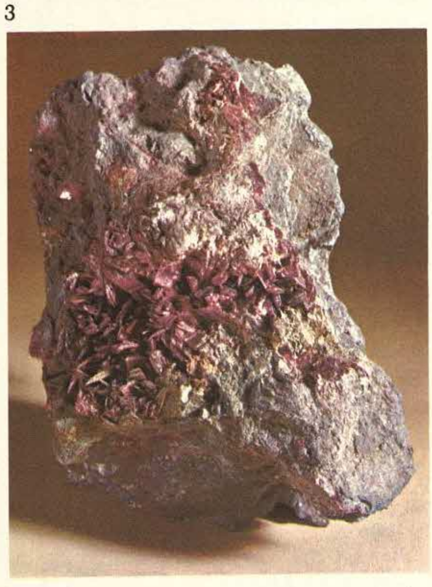
ORPIMENT—Known since ancient times, orpiment is one sulfide of arsenic. Its crystals are monoclinic, and are generally found as microcrystals. Bright yellow in color, orpiment has an almost metallic luster and turns red when heated.

2



REALGAR—This mineral, also an arsenic sulfide and monoclinic in crystalline form, is characterized by its red color and metallic luster. Realgar was widely used as a pigment during the Middle Ages.

3



ERYTHRITE—Also known as cobalt bloom, erythrite is formed by the oxidation of cobalt arsenide. It is an arsenite with the formula $Co_3(AsO_4)_2 \cdot 8H_2O$, and is found throughout Europe.

4

SILVER ARSENATE—This illustration shows the brown-red silver arsenate precipitate that results from the reaction between arsenic acid and silver nitrate. The chemical behavior of the arsenates is similar to that of the phosphates.

in many respects behaves like a metal. It possesses a characteristic metallic luster, and conducts electricity to a moderate extent.

A third allotrope, black arsenic, is produced by passing arsine (AsH_3) gas through a heated glass tube. This amorphous form, however, is unstable, converting to the metallic form above 200° C (392° F).

In all probability, elementary arsenic is a tetratomic molecule arranged in tetrahedral form. The element is rather reactive. When heated in air, arsenic burns with a blue flame, evolving dense white, garliclike fumes of the trioxide. Most arsenic compounds are highly toxic, and extreme care must be exercised in their use.

The halogens attack arsenic readily, producing trihalides. Arsenic reacts with nitric acid to yield arsenic acid, but is inert in the presence of dilute or reducing acids. Arsenic alloys with many metals, and lead containing about 1 percent arsenic forms almost perfectly spherical shot. Copper and brass take on added hardness when small amounts of arsenic are added.

THE CHEMISTRY OF ARSENIC

Arsenic has valences of −3, +3, and +5, making it a typical member of the Group V elements. In the −3 state, arsenic forms arsine, a highly toxic gas. The compound oxidizes rapidly, and shows a similarity to ammonia (NH_3) and phosphine (PH_3).

Trivalent (+3) arsenic forms arsenious oxide or arsenic trioxide (As_2O_3 and As_4O_6, respectively). The trioxide, when dissolved in water, produces a weakly acidic solution, no doubt due to the formation of a hydroxide, $As(OH)_3$, or arsenious acid, H_3AsO_3. These compounds are amphoteric, reacting either as acids or bases. As an acid, arsenic produces trivalent salts; as a base, arsenites.

5

AMMONIUM ARSENOMOLYBDATE—An excess of ammonium molybdate added to a nitrated solution of arsenates yields a complex, yellow, crystalline precipitate of ammonium arsenomolybdate when boiled. This precipitate, with the formula $(NH_4)_3AsO_4 \cdot 12MoO_3$, dissolves in ammonia and alkaline solutions.

One of the qualitative tests for the presence of arsenic involves bubbling hydrogen sulfide (H_2S) through a solution of arsenate salts. The formation of a brilliant yellow precipitate of arsenic sulfide, As_2S_5, is a strong indication of the presence of arsenic.

One of the halides of trivalent arsenic is the trichloride, $AsCl_3$. This compound, like the other arsenic halides, is obtained by direct synthesis or by the action of hydrochloric acid on arsenic trioxide:

$$As_2O_3 + 6HCl \rightarrow 2AsCl_3 + 3H_2O.$$

Arsenic trichloride is a colorless, oily liquid, very poisonous, and unstable in air.

6

MAGNESIUM-AMMONIUM ARSENATE—This compound is the result of reacting magnesium chloride and arsenic acid in the presence of ammonium chloride and ammonia. It is used in the quantitative determination of arsenic acid.

Copper arsenites were once used as wallpaper dyes, called Scheele's green or Schweinfurt green. These compounds are no longer legal for such use because they are attacked by a mold (*Penicillium brevicaule*) that liberates poisonous arsine.

The major compounds of pentavalent arsenic are the pentoxide As_2O_5, arsenic acid H_3AsO_4, and the arsenate salts of

this acid. Like phosphoric acid, arsenic acid is tribasic, although somewhat weaker. It has oxidizing properties, and can liberate iodine from iodides.

Compounds of trivalent arsenic are distinguishable from those of pentavalent arsenic by treating them with silver nitrate solution. Trivalent arsenites form canary-yellow silver arsenite, Ag_3AsO_3, while the arsenates form silver arsenate, Ag_3AsO_4, a brownish-red compound.

Arsenic pentachloride may be formed when arsenic trichloride and chlorine react at low temperature; if so, the substance is unstable above −30° C.

7

GALLIUM ARSENIDE MONOCRYSTALS—The small object at the left in the illustration is a seed for the larger gallium arsenide crystals. This compound is of tremendous importance in the manufacture of transistors and semiconductor lasers.

PHYSIOLOGICAL PROPERTIES OF ARSENIC COMPOUNDS

The use of arsenic as a poison is legendary, its compounds having the dubious honor of being the fatal poison in a number of famous murder cases. Often, these compounds are tasteless. Today, however, analytical techniques are such that minute traces of the element can be detected.

While all arsenic compounds are poisonous to some extent, antidotes for accidental poisoning are readily available. These counteragents include calcium hydroxide, $Ca(OH)_2$, magnesium sulfate, $MgSO_4$, and ferric hydroxide, $Fe(OH)_3$, all of which form insoluble precipitates with arsenic. Generally, trivalent arsenic compounds are more poisonous than the pentavalent forms.

Some of the organic derivatives of arsenic deserve special mention. Derived from arsine, these compounds have the hydrogen atoms replaced with organic groups and halogens. Examples are some of man's first chemical weapons—methyldichloroarsine ($AsCl_2CH_3$) and diphenylchloroarsine $AsCl(C_6H_5)_2$—both used in World War I.

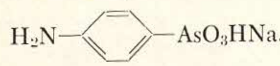
ARSENIC TRISULFIDE—When hydrogen sulfide is bubbled through an arsenic solution, the bright yellow precipitate of arsenic trisulfide results. In qualitative analysis, this is a standard test for arsenic. Orpiment is the mineral form of arsenic trisulfide.

8

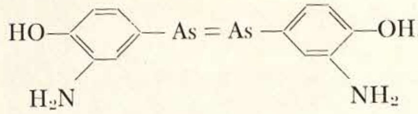
9

SILVER ARSENITE—Arsenious acid is produced when arsenic trioxide is dissolved in water. If silver nitrate is added to this solution, a canary-yellow precipitate of silver arsenite is formed. This test is used in qualitative chemical analysis to distinguish arsenious salts from arsenic salts, the latter producing a brownish-red precipitate.

Although arsenic compounds have been used as killers, certain arsenic compounds are life-savers. One example is sodium para-aminophenylarsenate, commonly called atoxyl:



It has been used to treat sleeping sickness since the day of the German physician and bacteriologist Robert Koch. Another medicinal use of arsenic is in the treatment of venereal disease. Koch himself called arsphenamine (trademark Salvarsan) a "magic bullet" in describing the manner in which it attacked and destroyed the syphilis spirochete. The formula of arsphenamine is



BISMUTH | pharmacology and metallurgy

1

BISMUTHINITE—The most important mineral of bismuth is this sulfide with the formula Bi_2S_3. The strata of the mineral shown here have a characteristic gray color and a metallic sheen.

This somewhat soft, crystalline metal, which resembles lead, is the last member of the Group VA elements. Though its discovery cannot be traced with accuracy, bismuth (Bi) may well have been known to some ancient civilizations—but confused with lead or antimony. In the mid-eighteenth century, the French apothecary and chemist Claude Geoffroy the younger demonstrated the metal to be distinct from lead. The name bismuth is generally recognized to come from the German *Weisse Masse,* meaning "white mass," later corrupted to *Wismuth.*

The element is not naturally abundant, but is found in both the elemental and combined states, notably as the sulfide and oxide. Important bismuth and bismuth compound deposits are found in South America, Korea, Australia, and Sweden. In the United States, the metal is obtained as a by-product of the refining of other metals, primarily lead, copper, tin, silver, and gold ores.

PREPARATION

Today, most of the world's supply of bismuth comes from the refining of other metals. However, it can be obtained by direct reduction of the mineral bismite, Bi_2O_3, with carbon. The oxide itself is a result of roasting the sulfide, bismuthinite, Bi_2S_3. Still another commercial source is the melting of a bismuth salt in association with alkalis and potassium cyanide. The typical reactions are:

$$2Bi_2S_3 + 9O_2 \rightarrow 2Bi_2O_3 + 6SO_2$$
$$Bi_2O_3 + 3C \rightarrow 2Bi + 3CO \qquad (1)$$

$$2BiOCl + 2KOH + 3KCN \rightarrow 2Bi + 2KCl + 3KCNO + H_2O. \qquad (2)$$

If obtained as a by-product of other metallurgical processes, refining to obtain pure bismuth involves solution of the impure metal in nitric acid, followed by electrolysis of the nitrate.

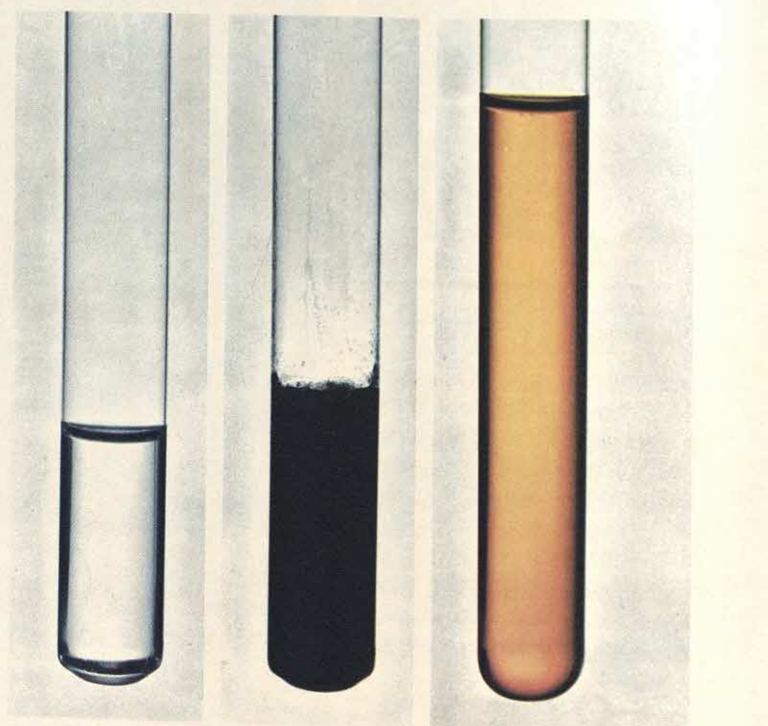
In the pure state, bismuth is a white, crystalline solid with a pinkish tinge. Like antimony, which precedes bismuth in Group VA, it is a brittle metal and has a relatively low melting point. Its coefficient of thermal conductivity is the lowest of any metal except mercury, and bismuth has a very high electrical resistance.

CHEMICAL PROPERTIES

All of the VA elements (nitrogen, phosphorus, arsenic, antimony, and bismuth) have five electrons in their outermost shell. Thus, it would appear that all would have a +3 valence in the most stable state. Such is not the case, however, for the first four elements in the group can achieve stability either by giving up some or all of the five electrons, or by gaining three to complete the shell. Bismuth demonstrates its greatest stability in the +3 state, though it also exhibits a +5 valence. Furthermore, bismuth is the most metallic of the elements in this group.

A CHARACTERISTIC REACTION OF BISMUTH—The test tube in Illustration 2a contains a solution of bismuth nitrate. By adding potassium iodide, a simple exchange reaction occurs and a black precipitate of bismuth iodide is formed (Illustration 2b). If an excess of the potassium iodide is added to the precipitate, it dissolves to become the complex $(BiI_4)^-$ ion (Illustration 2c). Such a reaction is used in analytical chemistry to test for the presence of bismuth.

2a 2b 2c



3

BASIC BISMUTH NITRATE—Sometimes called bismuth magistery, this is one of the most common bismuth compounds. It is used in making cosmetics and also has medical applications.

At normal room temperatures, bismuth does not oxidize, although heating causes the trioxide to form. The metal is readily dissolved by nitric and sulfuric acids to form the respective nitrate and sulfate, but reacts with the halogen acids only when the solutions are hot. In this context, bismuth combines readily with the halogens, forming the appropriate salts by direct reaction.

COMPOUNDS OF TRIVALENT BISMUTH

Bismuth oxide, Bi_2O_3, is a yellow-brown powder that results from the burning of the metal. The oxide is also a product of the heating of bismuth salts to red heat:

$$Bi_2(CO_3)_3 \xrightarrow{\Delta} Bi_2O_3 + 3CO_2.$$

The oxide is stable and insoluble in either water or alkaline solutions. The compound will dissolve in acids, on the other hand, forming Bi^{3+} or BiO^+ ions.

Bismuth hydroxide, $Bi(OH)_3$, cannot be prepared from the oxide because of the latter's insolubility in water or bases. This compound is obtained by reacting a bismuth salt ($BiCl_3$, for example) with an alkali in the absence of heat.

Bismuth forms compounds with all of the halogens, either by direct synthesis or by reacting the metal or its salts with the appropriate acids. For example, the chloride can be made directly from the elements or by treating bismuth oxide with hydrochloric acid. Third, dissolution of the metal in aqua regia gives the same result. In any case, the chloride is rather unstable, and dissolves in water to form the hydroxychloride $Bi(OH)_2Cl$. The chloride also dissolves in organic solvents.

Bismuth fluoride is produced by evaporating the product of the reaction between the oxide and hydrofluoric acid. This compound, unlike the chloride, is quite stable, with a melting point in excess of 725° C (1,337° F). While insoluble in cold water, it dissolves in many inorganic acids. Both the bromide and iodide can be prepared by treating a bismuth salt with the alkali halides.

Another important salt of trivalent bismuth is the nitrate, $Bi(NO_3)_3 \cdot 5H_2O$. This compound is extremely hygroscopic, rapidly hydrolyzing to the basic nitrate, $BiONO_3 \cdot H_2O$. The basic nitrate finds use in medicine, as does the sulfate. Certain compounds used to combat indigestion contain these bismuth salts.

While most bismuth compounds are formed by the trivalent ion, a small number of pentavalent materials exist. These are generally unstable, and they have limited use. Examples worth noting are the pentafluoride and the pentoxide. The latter is used as an oxidizer in analytical chemistry.

USES OF BISMUTH AND ITS SALTS

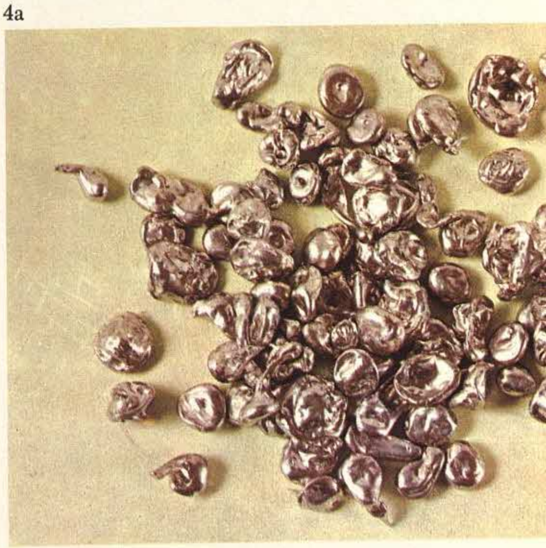
One of the most common uses of this metal is in alloys with low melting points. Ordinary electrical fuses are everyday examples of this application. The most widely used bismuth alloys are Rose metal, composed of two parts Bi, one part Pb, and one part Sn; its melting point is 93.7° C (about 199° F). Another bismuth alloy is Wood's metal, composed of four parts Bi, two parts Pb, one part Cd, and one part Sn; its melting point is 65.5° C (about 149° F). A third alloy is Newton's metal, composed of eight parts Bi, five parts Pb, three parts Sn; its melting point is 94.5° C (about 201° F).

Pharmaceutically, bismuth compounds have been used since the sixteenth century. Particularly, the compound known as bismuth magistery—the basic nitrate—was used indiscriminately and perhaps caused more harm than good. In general, bismuth salts are astringent and are harmless in small quantities because the human body eliminates them faster than they can be absorbed. However, before barium replaced bismuth in radiology, the large quantities of bismuth salts necessary for x-ray examination were the cause of severe poisoning.

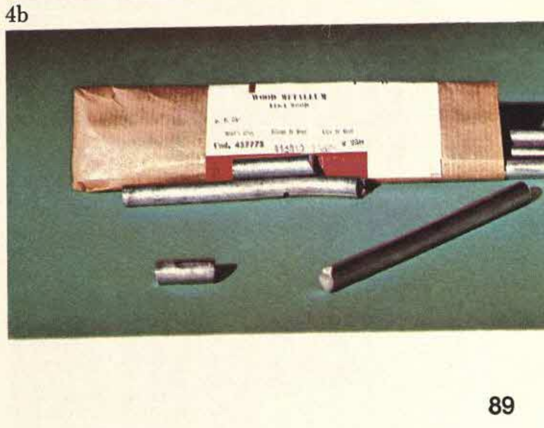
Organic bismuth compounds are used as medicants for wounds and in burn treatment.

LOW MELTING ALLOYS—One of the primary uses of bismuth is in alloys that melt at very low temperatures, many below 100° C (212° F). Rose metal (Illustration 4a) is composed of bismuth, tin, and lead in the ratio 50:25:25, and has a melting point of 93.7° C (about 199° F). The alloy in Illustration 4b is Wood's metal, with a melting point of 65.5° C (about 149° F). Its composition is 50 percent bismuth, 25 percent tin, and 12.5 percent each of lead and cadmium.

4a



4b



TIN | the metal that cries

Known to the ancients, the element tin was obtained in a relatively pure form and used in making alloys, particularly bronze. Egyptian bronzes dating back to 2000 B.C. are not uncommon, but tin was undoubtedly known much earlier. The symbol of tin, Sn, comes from the Latin *stannum.*

Elementary tin is not too common in the Earth's crust, although the oxide, cassiterite, is quite abundant and fairly widespread. Considerable amounts of the mineral were mined by the Phoenicians in England, but the true growth of the tin industry began around 1500 at these ancient mining sites. Today, most of the world's supply of the element is found in Malaya, Bolivia, Indonesia, the Democratic Republic of the Congo, Nigeria, and Thailand.

Cassiterite, SnO_2, is the primary ore of tin, and the compound is found as tetragonal crystals. In nature, because of iron impurities, the normally white oxide is darkly colored. To extract the metal, the sand containing the cassiterite is enriched and roasted at a temperature above 1,100° C (2,012° F) to remove sulfur and arsenic impurities. The mass is then reduced with carbon in a reverberatory kiln to obtain the elementary material:

$$SnO_2 + C \rightarrow Sn + CO_2.$$

The remaining slag, from which the tin has been separated, is reworked in a similar manner to recover as much of the metal as possible. Finally, the tin is refined at lowered temperatures such that any remaining impurities collect as lumps that are readily separated from the molten metal.

Elementary tin is a silver-white, crystalline metal with a low melting point of 231.9° C (about 450° F). Its crystalline structure is revealed by washing the metal with hydrochloric acid, and it is the breaking of the crystals that causes the metal to "cry" when a bar is bent. Because it is quite ductile and malleable, tin can be drawn into fine wire and rolled into thin sheet—the familiar tinfoil.

There are three crystal modifications of the element, known respectively as α tin (cubic, gray), β tin (tetragonal, white), and γ tin (rhombic, white to silvery). The phase in which the metal is found is dependent on temperature:

$$\alpha Sn \xrightarrow{13.2°} \beta Sn \xrightarrow{161°} \gamma Sn \xrightarrow{232°} Sn\,(\text{liquid}). \quad (1)$$

Both the alpha and beta modifications have very compact atomic structures, the latter having a density greater by a factor of about 0.5 due to a more compact atomic arrangement.

At low temperatures, white tin changes to the gray form, although it may exist in a metastable phase even at 0° C (32° F). However, the presence of even trace amounts of the gray variety will catalyze the transition and turn an entire mass of tin to powder over a period of time. This phenomenon is called "tin pest" or "tin disease," and the results of this transformation can be seen on the organ pipes in old cathedrals. At the low winter temperatures encountered in unheated churches, the tin pipes developed cancer-like growths. Originally, these were attributed to the devil, then to microorganisms. Now, however, the destruction is known to have been caused by a simple change in structure.

At ordinary temperatures, tin is a stable metal in air. Intense heating, however, causes the metal to burn with an intense light accompanied by the forma-

TIN AND ITS MOST IMPORTANT MINERAL—Illustration 1a shows tin crystals under polarized light. (130 X) The dark crystals in Illustration 1b are cassiterite, the most important tin mineral. The ordinarily white oxide is colored by the presence of iron impurities. Such impurities often give rise to twinning—the association of two or more crystals of the same species. The specimen in Illustration 1c is cassiterite with quartz, from a deposit in Cornwall, the site of ancient Phoenician mines.

1a

1b

1c

tion of cassiterite, SnO_2. The metal is soluble in both acids and bases. For example, treatment with hydrochloric acids produces a chloride by simple exchange. In alkaline solutions, stannates are formed with a concurrent evolution of hydrogen. Solutions of stannous salts, when reacted with zinc, form metallic tin with an unusual needle-shaped structure.

The oxidation states of tin are +2 and +4, and the element is a member of Group IVA in the periodic table.

USES

Because it exhibits good resistance to ordinary reagents, tin is widely used to plate base metals for protection and to make specialized containers. The familiar tin can is iron sheet plated with a thin coating of tin. This forms a protective barrier against the action of most solutions used in the preservation of food because of the formation of a passive oxide on the tin. However, should the tin plate be scratched or otherwise damaged, the underlying iron corrodes very rapidly due to galvanic action.

In thin sheets (tinfoil), the metal was used for many years for making mirrors and as a wrapper for foodstuffs. Foil is also used extensively in the electronics industry as a compact form of electrical conductor.

A considerable amount of tin is used to make alloys. Solder, for example, contains almost equal portions of tin and lead, and the mixture melts at a temperature considerably lower than that of the components.

As an amalgam with mercury, tin can be plated on glass and as such is used to make Venetian mirrors. Alloyed with metals such as antimony and zinc, tin forms a fusible metal used for making bearings and mountings.

Because of its unique properties, tin is used more widely than any other metal.

BRONZES

Discovered by the ancients, bronze is a yellow-gold alloy of tin and copper and has given its name to a prehistoric time—the Bronze Age.

Copper containing up to 10 percent tin creates an alloy that is very resistant to corrosion, is malleable, and possesses good mechanical properties. Tin in percentages above 10 percent increases the mechanical properties but decreases malleability.

One of the most common and important of the bronzes is bell metal. Composed of copper (75 percent), tin (25 percent), and traces of lead and zinc, this alloy has a gray color, melts easily, has a fine granular structure, but is somewhat fragile. However, the metal is quite hard and has excellent resonant qualities.

Other bronzes, each with characteristic applications, are: gunmetal (90 percent copper, about 10 percent tin, and traces of zinc); phosphor bronze, made from ordinary bronze with a trace of phosphorus, is harder than the simple alloy and is used to make materials with high tensile strength; and a type of bronze containing 5 percent zinc and 2 percent lead used for decorative purposes. The last can be worked with a chisel, and readily forms a patina that simulates ancient bronze.

COMPOUNDS OF TIN

The two valences of tin, +2 and +4, form stannous and stannic compounds, respectively. Stannous oxide, SnO, is a black powder that readily oxidizes to white stannic oxide, SnO_2, at normal temperatures. Corresponding to the +2 oxide is stannous hydroxide, easily obtainable from the reaction between stannous chloride and sodium hydroxide:

$$SnCl_2 + 2NaOH \rightarrow Sn(OH)_2 + 2NaCl.$$

Adding an excess of the sodium hydroxide causes the formation of sodium stannite:

$$Sn(OH)_2 + 2NaOH \rightarrow Na_2SnO_2 + 2H_2O.$$

Stannous sulfide, SnS, is a dark brown precipitate resulting from the reaction between a solution of stannous chloride and hydrogen sulfide. This reaction is sometimes used as a qualitative test for tin.

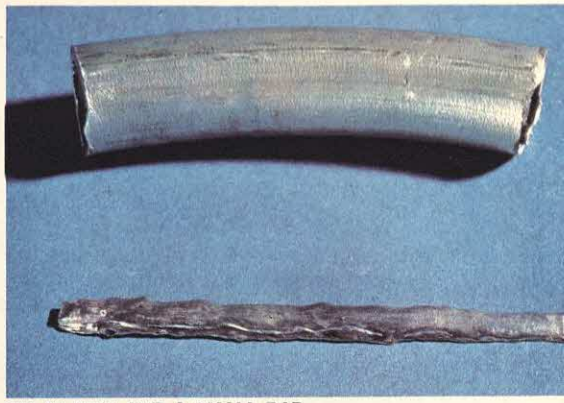
In the +4 state, tin oxide is the familiar cassiterite, SnO_2. Found naturally, it can also be prepared by burning elemental tin in air. This compound, when fused with sodium hydroxide, forms the corresponding stannate, Na_2SnO_3.

Stannic chloride, $SnCl_4$, is a liquid that fumes strongly when exposed to air. It is formed easily by direct synthesis of the elements. Added to hydrochloric acid, stannic chloride produces chlorostannic acid:

$$SnCl_4 + 2HCl \rightarrow H_2SnCl_6.$$

The double salt, $SnCl_4 \cdot 2NH_4Cl$, is widely used as a mordant in the textile industry.

Stannic sulfide can be formed by the reaction of stannic salts with hydrogen sulfide. This yellow amorphous mass, when in the form of light, gold-colored sheets produced by sublimation, is called mosaic gold. It has been used for artificial gilding.



TIN AS PIPE AND A SMALL BAR

A quantitative test for stannic salts involves treating a solution of the salt (the chloride, for example) with a measured quantity of auric chloride, $AuCl_3$. This results in the formation of a negatively charged stannic acid hydrosol that, by co-precipitating with the positively charged gold hydrosol, creates a purple-red suspension.

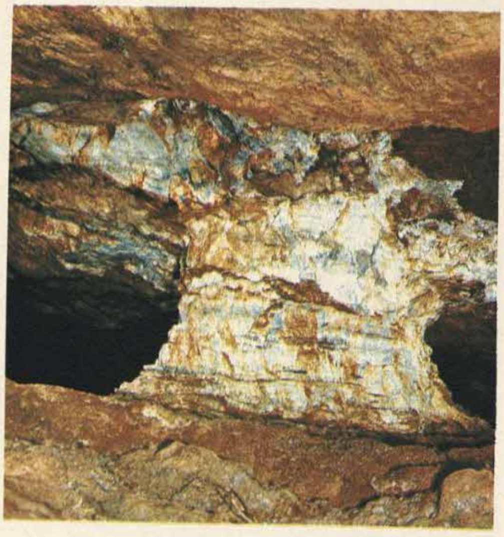
MIDDLE BRONZE AGE WEAPONS, CIRCA 1500 B.C.

STRONTIUM AND BARIUM | more curious than important

Strontium (Sr) and barium (Ba) are members of the alkaline-earth family of elements, and share their membership with beryllium, calcium, magnesium, and radium. "Alkaline" refers to a similarity of chemical characteristics demonstrated by the alkali metals, while "earth" derives from the alchemical term for substances insoluble in water. The latter is a property of several barium and strontium compounds.

The history of barium dates from 1770 when the Swedish chemist, Carl Scheele, while working with manganese dioxide, discovered a mineral that exhibited unique chemical properties. By reacting impure manganese dioxide with sulfuric acid, Scheele produced a heavy white precipitate, but was unable to explain its origin. Because this new compound was highly insoluble, he called the impurities in the manganese dioxide "heavy earth." Ten years later, one of Scheele's students found the impurities to be carbonate, which he called "witherite." The term "heavy earth" was changed to barium (from the Greek word *barys* meaning "heavy"). Not until 1808, however, was the metal isolated for the first time, by the English chemist Humphry Davy.

BARITE MINE—This illustration shows an almost vertical pillar of stratified barite at a depth of about 2,000 m (about 6,700 ft). The most commercially important barite deposits are in Germany, England, and the United States.



The history of strontium somewhat parallels that of barium. Its existence was deduced by the Scotsman Thomas Hope in 1790. While studying some minerals found at Strontian in Argyll, Scotland, Hope discovered a compound similar in many ways to witherite (barium carbonate), the only difference being the unknown's reaction with hydrochloric acid. He correctly surmised that a new element, similar to barium, was responsible for a product differing from barium chloride. Shortly thereafter, Davy successfully isolated and studied strontium and delineated those few chemical characteristics that distinguish it from barium.

BARIUM

Of those elements having atomic numbers greater than 100, barium is the most common in the Earth's crust. It is found primarily as barite ($BaSO_4$) and witherite ($BaCO_3$). The carbonate, when treated with appropriate acids, is the major source of barium salts.

Barium not only occurs as mineral ores, but is also found in appreciable quantities in certain plants. Oak leaves, for example, contain up to 0.3 percent of the metal. Because its soluble salts are poisonous to animal life, barium compounds are not found naturally in the Animal Kingdom. Its insoluble salts, however, are used medically, to render the digestive system opaque to x-rays.

The list of other applications for barium compounds is confined primarily to pigments, insecticides, rodenticides, and electronics.

Metallic barium can be produced by the electrolysis of its fused chloride:

$$3BaO + 2Al \rightarrow 3Ba + Al_2O_3;$$

or by the reduction of the oxide with aluminum or silicon:

$$3BaO + Si \rightarrow 2Ba + BaSiO_3.$$

The element is soft, and when pure resembles lead. Because it oxidizes readily, it is generally stored under petroleum, or some other suitable medium, to exclude the atmosphere.

BARITE—Barium sulfate is the most important barium mineral. It crystallizes and may appear as magnificent, many-faceted crystals, as fibrous blocks, or in compact masses.

Metallic barium is used in the manufacture of radio vacuum tubes. It removes the final traces of gaseous elements remaining after the tubes have been evacuated almost completely by other methods. It is also used to remove oxygen in the refining of copper. It is a constituent of several alloys, one of the most important of which is Frary metal, a bearing or antifriction metal that contains lead and calcium as well as barium. An alloy of nickel and barium, which readily emits electrons when heated, is used for this reason in radio tubes and in the points of spark plugs.

The metal is difficult to isolate. Davy first tried to electrolyze baryta (barium oxide) but was unsuccessful; later attempts were made by him using barium chloride in the presence of mercury. In this way he obtained an amalgam, from which on distilling off the mercury the barium was obtained as a silver-white residue.

The commercial production of barium depends on the electrolysis of fused barium chloride or the reduction by aluminum of a mixture of barium monoxide

and barium peroxide in a vacuum furnace that is heated electrically.

Barium and its salts can be readily detected by the yellowish-green color they give off when moistened with hydrochloric acid and heated in the Bunsen flame, or by observation of their spectra, when two characteristic green lines are seen. In solution, barium salts may be detected by the immediate precipitate they give on the addition of calcium sulfate, and by the yellow precipitate of barium chromate formed in the presence of dilute acetic acid on the addition of potassium chromate.

Characteristically, barium exhibits a +2 oxidation state, as do the other members of the group IIA elements.

BARIUM COMPOUNDS

Barium oxide, BaO, is commercially produced by roasting the nitrate in special crucibles. However, the porous oxide is more efficiently manufactured by treating barium carbonate with carbon:

$$BaCO_3 + C \rightarrow BaO + 2CO.$$

This compound is a white powder similar to the analogous calcium and strontium oxides. Like them, barium oxide crystallizes in a center-faced cubic lattice. It reacts strongly with water to form the hydroxide, $Ba(OH)_2$, and while its uses are limited, the oxide is sometimes used to extract sugar from molasses.

The hydroxide is a strong base and, like the oxide, can be used in the sugar industry.

When barium oxide is heated strongly in an oxygen atmosphere, the resulting product is barium peroxide, BaO_2. In crude form, the compound is pale green, but is colorless when pure. In either case, barium oxide is a strong oxidizing agent that releases oxygen when heated.

Barium chloride, another important compound, results from the fusion of barium sulfide and calcium chloride:

$$BaS + CaCl_2 \rightarrow BaCl_2 + CaS.$$

A second production method incorporates the roasting of barite with calcium chloride in the presence of carbon as a reducing agent.

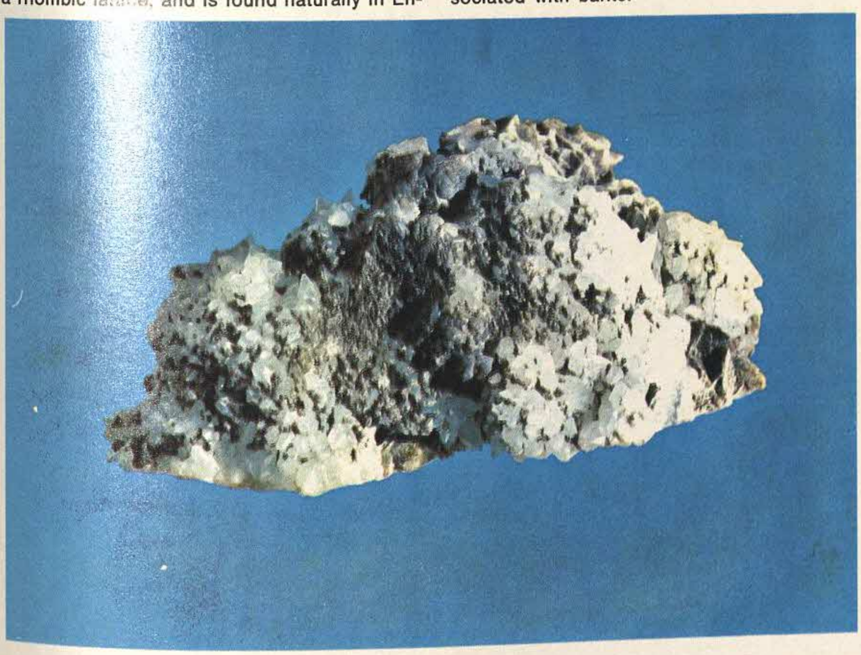
Barium chloride is soluble, and therefore poisonous; it crystallizes with two molecules of water ($BaCl_2 \cdot 2H_2O$). Although similar in structure to calcium chloride, this compound is not hygroscopic. Primarily, barium chloride is used to prepare the more important sulfate, and as a purifier in the chlorine and soda industries. It is also used as a flux in magnesium alloys.

Barium sulfate is found naturally as barite (heavy spar), and is one of the most highly insoluble compounds known. Chemically, the sulfate is easily prepared by reacting any soluble barium salt with sulfuric acid. In its purified form, barium sulfate is used in x-ray examination of the digestive tract—its insolubility making it nonpoisonous and its high molecular weight rendering it opaque to x-rays. Mixed with zinc sulfide, barium sulfate is used as the white pigment lithopone. This material has excellent covering qualities, and is not darkened on exposure to sulfides. In addition, its virtual insolubility makes it an excellent substitute for paints based on white lead pigments that are highly poisonous.

A major use of barium sulfate is in the petroleum industry, where it is a constituent in the mud used to facilitate well drilling. The mud is pumped down into the well through the pipe attached to the rotary drill bit; it serves to carry rock fragments back up to the surface, to cool and lubricate the bit, and also to prevent collapse of unstable strata into the hole. Drilling mud is composed of clay minerals and water, along with some special

URANOCIRCITE—This attractive mineral crystallizes in a tetragonal system. It is a barium-uranyl phosphate with the formula $Ba(UO_2, PO_4)_2 \cdot 8H_2O$.

WITHERITE—Barium carbonate crystallizes in a rhombic lattice, and is found naturally in England and the Soviet Union. It is sometimes associated with barite.



chemicals such as barium sulfate, depending on the composition of the water and the rock or soil strata being drilled.

Some barium sulfate is used as a body or filler in the manufacture of certain kinds of cloth and paper.

Barite or heavy spar was first investigated in 1602 by Vincenzo Cascariolo, a shoemaker of Bologna. He discovered that after ignition with combustible substances the barite became phosphorescent; for this reason it has sometimes been called Bolognian phosphorus.

In the glass industry, barium carbonate (naturally occurring witherite) has some applications. This compound loses carbon dioxide only at temperatures exceeding 1,350° C (2,462° F).

Finally, barium nitrate is used in the preparation of other barium salts, notably the peroxide. This salt imparts an emerald-green color to flame, and is used in pyrotechnics.

STRONTIUM

Strontium is distributed in small quantities in many different rocks and soils on the Earth's surface. Some is present in bones, in which it replaces small amounts of calcium. Because calcium and barium, which closely resemble strontium, occur in much greater abundance, the element strontium has not been produced in quantities that are commercially important.

While not as widespread as barium, strontium occurs naturally as celestite ($SrSO_4$) and strontianite ($SrCO_3$). Chemically, strontium's properties are similar to those of barium and calcium. It is a softer metal than calcium but decomposes water more vigorously. The metal can be prepared by heating strontium chloride with a sodium amalgam, followed by distillation of the mercury. One commercial method used to prepare the metal employs the reduction of strontium oxide with silicon:

$$3SrO + Si \rightarrow 2Sr + SrSiO_3.$$

When freshly cut, strontium has a silvery luster. This becomes yellow quickly, however, due to the formation of the oxide. Finely divided strontium burns spontaneously in air, producing a brilliant red flame.

The oxide and hydroxide of strontium have properties analogous to the barium compounds, while strontium chloride is less soluble than its calcium counterpart.

Strontium sulfate (celestite) is isomorphous with barite (barium sulfate), but is somewhat more soluble. Strontium carbonate (strontianite) is isomorphous with calcium carbonate and is only slightly soluble in water.

Unlike soluble barium salts, strontium compounds are not toxic in a chemical

CELESTITE—This mineral forms a rhombic crystal lattice and is isomorphous with barite, although it is not as common. Often it occurs in the form of many-faceted crystals, and it may be associated with sulfur, gypsum, and calcite. The specimen illustrated is fluorescing under ultraviolet radiation.

sense. However, one of strontium's isotopes presents what scientists believe to be a serious threat to human health.

STRONTIUM-90

There are four stable isotopes of the element; their mass numbers, in the order of abundance, are 88, 86, 87, and 84. Several radioactive isotopes are produced by nuclear reactions. Of these, the isotope having a mass number of 90 has received the most attention because of its presence in the radioactive fallout from nuclear explosions. This has aroused concern because strontium-90 remains radioactive for a relatively long period of time; it has a half-life of 28 years.

Along with other fallout material, strontium-90 may be deposited on the foliage of plants, on the soil, or on the sea. Because it is chemically similar to calcium, the radioactive substance may be incorporated into plants and eventually find its way into plant and animal foods eaten by humans. Milk and drinking water may contain strontium-90. In the sea, strontium-90 becomes concentrated in the skeletons of fishes and in aquatic plants.

In the human body, strontium-90 becomes concentrated in bone. Newborn babies, who have actively growing bones, retain relatively greater amounts of the radioactive substance than do adults.

STRONTIANITE—The most common minerals of strontium are celestite ($SrSO_4$) and strontianite ($SrCO_3$). As shown in the illustration, strontianite crystallizes in a rhombic lattice. This mineral is isomorphous with witherite and other carbonates.

MERCURY | the liquid metal

One of the most unique of the natural elements, mercury (Hg) was known to the ancient Chinese and Hindus, was mentioned by Moses in the Pentateuch, and was used by the Egyptians to make an amalgam with copper perhaps as early as 1500 B.C. The Greek philosopher Theophrastus described "quicksilver" and its preparation from the mineral cinnabar in the third century B.C.

The chemical symbol for mercury, Hg, is derived from the word *hydrargyrum* (the Latin word meaning "liquid silver"), given the element by Dioscurides in his *De materia medica* around the beginning of the Christian era.

In his *Historiae naturalis,* Pliny made a distinction between quicksilver and *hydrargyrum,* the first referring to mercury in its native state and the second to mercury produced by refining of ores.

The name mercury came into use at the beginning of the Middle Ages when alchemists derived it from the name of the swift messenger of the gods of Roman mythology. During this period of history, mercury enjoyed the important role of being the "father" of all metals, according to the alchemists. It is interesting to note the alchemists' determination to transmute mercury into gold, solely on the basis that the two metals are difficult to separate. Naturally, they could not have known that the atomic numbers for these elements differ by only one unit and that the mass number of gold lies between that of mercury's two stable isotopes. (Theoretically, if a modern chemist wanted to prepare gold by nuclear reaction, the simplest way would be to properly bombard mercury.)

Mercury is the only metallic element that is liquid at room temperature (although cesium, gallium, and rubidium can be liquid near normal temperatures). Only rarely is the element found in a free state. Rather, it is almost exclusively found as the sulfide in the mineral cinnabar, HgS. More than half of the world's supply of mercury is obtained from cinnabar mined in Spain and Italy.

FROM PLINY'S *HISTORIAE NATURALIS*—This valuable first-century work provides great insight into the scientific thought of the time. In it, Pliny made the seemingly unnecessary distinction between *hydrargyrum* (for mercury obtained from ores) and "quicksilver" (for the element in its natural state).

CINNABAR—Most of the world's mercury is derived from cinnabar. The sulfide is found in microcrystalline masses varying in color from red to dark brown, although on occasion it is seen as many-faceted crystals having a diamondlike sparkle.

PREPARATION

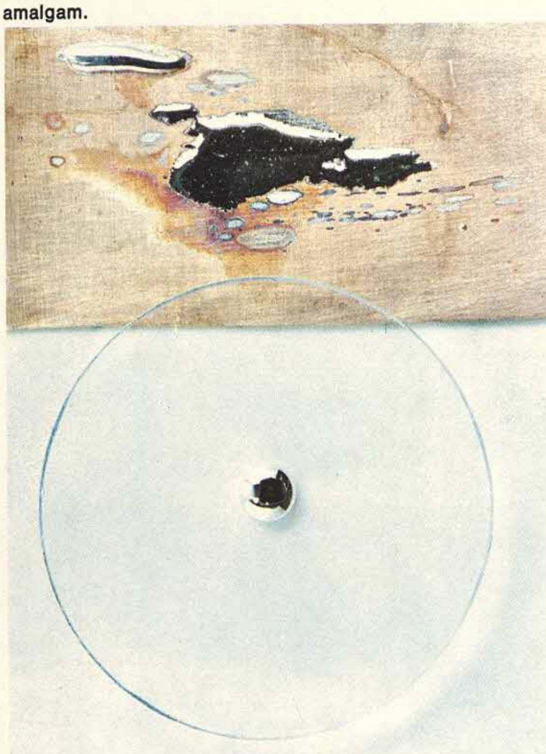
The primary method for preparing elemental mercury is the roasting of cinnabar in an air stream and subsequent condensation of the vapor. The sulfur dioxide evolved is easily soluble in water, resulting in a relatively pure metal. However, further heating and distillation remove trace impurities of lead, copper, and gold. In the pure state, mercury flows with ease.

CHEMICAL AND PHYSICAL PROPERTIES

The liquid metal is silvery and quite heavy. Mercury is a poor conductor of heat; its electrical conductivity is only fair compared to that of other metals.

The metal is stable in air, although at its boiling point of 356.9° C (about 675°

MERCURY AND THE FORMATION OF AN AMALGAM—On the watch glass the blob of silvery mercury will remain inactive. In contact with copper, however, the two metals will combine over a period of time to form an amalgam.



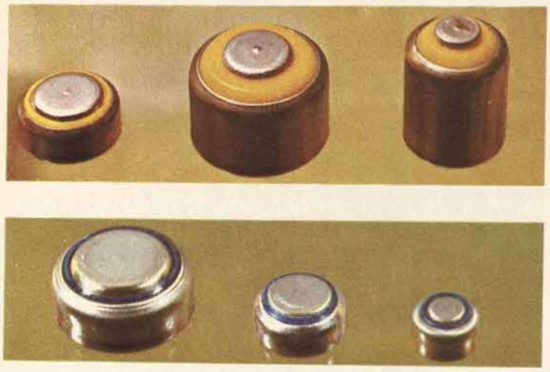
F) it becomes covered with a red layer of mercuric oxide. Mercury readily combines with the halogens, and dissolves a number of other metals to form amalgams. Some of these are true compounds (Na_2Hg, for example), while others are more correctly called mixtures ($AuHg$, $AgHg$, and $PbHg$, for example).

Mercury is quite volatile, and highly toxic. Strict safety precautions must be observed when using the metal or its compounds, and adequate ventilation is necessary. Mercury poisoning is insidious, with many bizarre symptoms both physical and psychological.

Chronic mercury poisoning results from exposure to small amounts of mercury over extended periods of time, as may occur in industries that use mercury or its salts. The symptoms include loss of appetite, salivation, gingivitis, nutritional disturbances, increasing renal damage, and anemia.

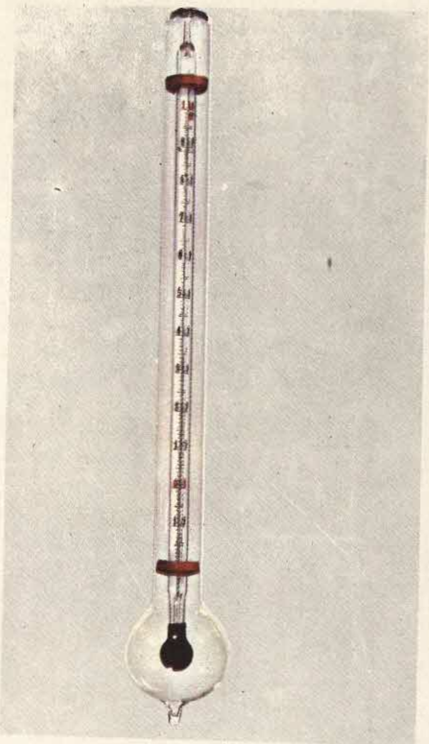
PRINCIPAL USES OF MERCURY AND ITS COMPOUNDS

Mercury finds use in a wide range of industries and products, notably in electronics, pharmaceuticals, and metallurgy. Familiar evidence of the metal's use can be seen in thermometers and barometers, in mercury lamps with their characteristic blue glow, and in silent electrical switches. In laboratories, mercury is used in vacuum pumps and for electrodes, while the metals industries use it to extract silver and gold. The powerful explosive mercury fulminate is a metal-organic compound; some of the inorganic salts of this compound are used in the treatment of disease.

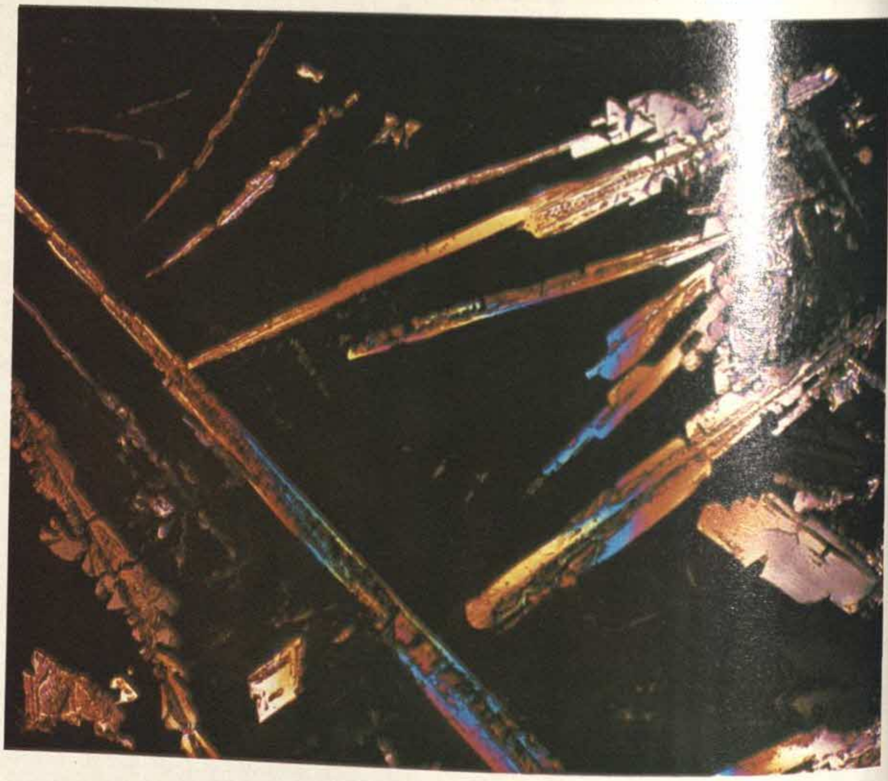


MERCURY BATTERIES—The top illustration shows some types of mercury batteries used in photographic exposure meters, while those in the bottom illustration are often used in hearing aids. Mercury batteries are noted for their long life.

RUMFORD VACUUM THERMOMETER — This specialized piece of equipment is made up of a mercury thermometer enclosed in an evacuated tube. It is used to demonstrate the rapid propagation of radiant heat under airless conditions.



CORROSIVE SUBLIMATE — These normally colorless crystals of mercuric chloride are seen under polarized light. (130 X) Industrially, the compound is produced by direct synthesis from the elements. In dilute solution, this highly toxic salt has antiseptic properties.



All mercury compounds should be considered highly poisonous, especially those that are soluble in water. Nonetheless, some of these are used to treat skin disorders. The two valence states of the element produce mercurous (+1) and mercuric (+2) compounds.

Mercurous salts include the oxide, Hg_2O, which is easily formed by precipitating any mercurous compound in sodium hydroxide. The better-known chloride, or calomel, is produced by the reduction of mercuric chloride with mercury:

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2.$$

This white compound is photosensitive, and when exposed to light reverses the above reaction to yield black metallic mercury and mercuric chloride. Calomel is used as an electrode in certain analytical apparatus, and for coloring porcelain when mixed with gold. In ultra-pure form, calomel is used in medicine.

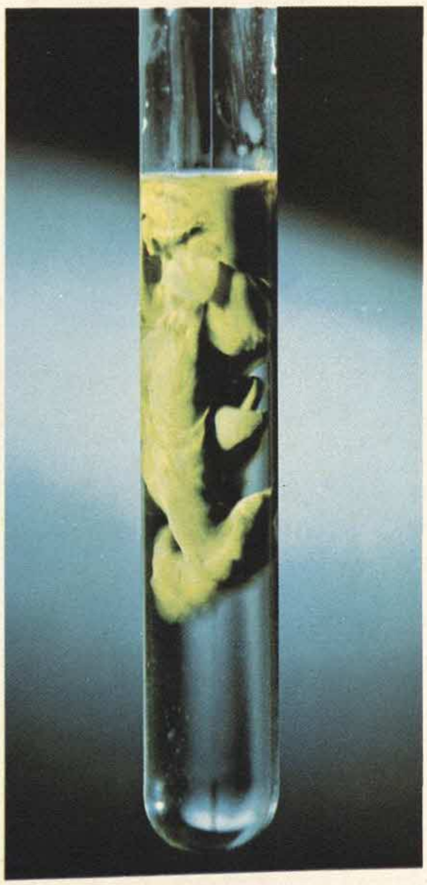
One of the most toxic of the mercury compounds is mercurous nitrate, produced in the reaction between the metallic element and nitric acid. This salt is little used outside the analytical laboratory.

Most of the important mercury compounds are formed in the +2 oxidation state. Among these mercuric compounds is mercuric oxide, HgO, also called red precipitate. It is easily prepared by heating the metal or mercuric nitrate, and is a very fine, bright, brick-red compound sometimes used as artist's pigment. Interestingly, if mercuric oxide is formed in a "wet" reaction, as in the reaction of a mercuric salt with sodium hydroxide, the compound is bright yellow that turns dark as black metallic mercury separates. This variation in the color of the oxide is not due to polymorphism, but to a difference in particle size.

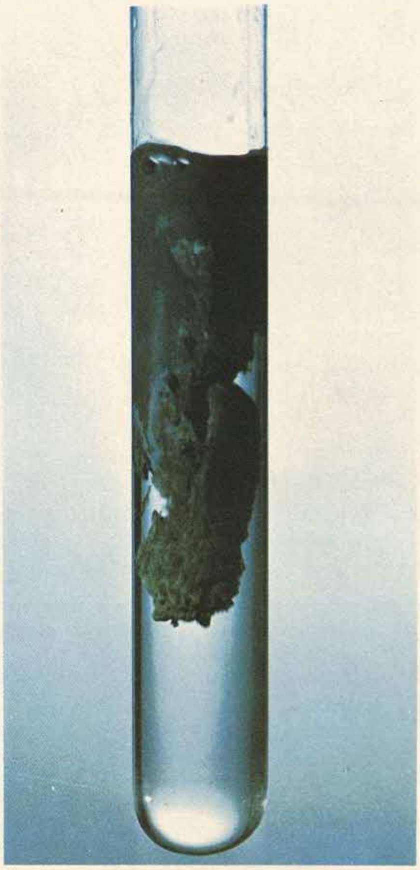
Mercuric chloride, also known as cor-

MERCURIC OXIDE—The billowy precipitate is mercuric oxide, formed as a result of the reaction between mercuric chloride and potassium hydroxide.

MERCUROUS ION REACTION—The lime-green precipitate is mercurous iodide. Traces of metallic mercury give it this color—it is normally yellow in the pure state.



CHARACTERISTIC MERCURIC ION REACTION—Potassium iodide added to a solution of mercuric chloride produces the brick-red precipitate of mercuric iodide.



FORMATION OF MERCURY AND MERCURY AMMONIUM NITRATE—This reaction provides a useful method for detecting trace presence of ammonia in water. The black precipitate is produced when mercurous nitrate is added to an ammonia solution.

rosive sublimate, is a violent poison, and is sometimes used as an antiseptic. This salt is prepared by sublimating a mixture of mercuric sulfate and sodium chloride to which manganese dioxide has been added as a catalyst.

Mercuric iodide, a precipitate resulting from the reaction between a mercuric salt and potassium iodide, is a yellow, crystalline compound with a dual personality. Once formed, the yellow salt quickly turns red, but returns to the yellow form at 130° C (266° F), only to melt into a red mass at 223° C (about 431° F). Such color changes are due to various allotropic forms of the substance.

In an excess of iodide, mercuric iodide dissolves, and the resulting solution is called Nessler's reagent. This is used to detect minute amounts of ammonia, in which it forms a yellow precipitate, and which can be used to determine levels of water pollution.

The sulfide from which mercury itself is produced is a mercuric compound. In the laboratory, HgS can be prepared by direct synthesis from the elements. The red powder of mercuric sulfide provides vermilion, one of the most vivid reds in the artist's palette.

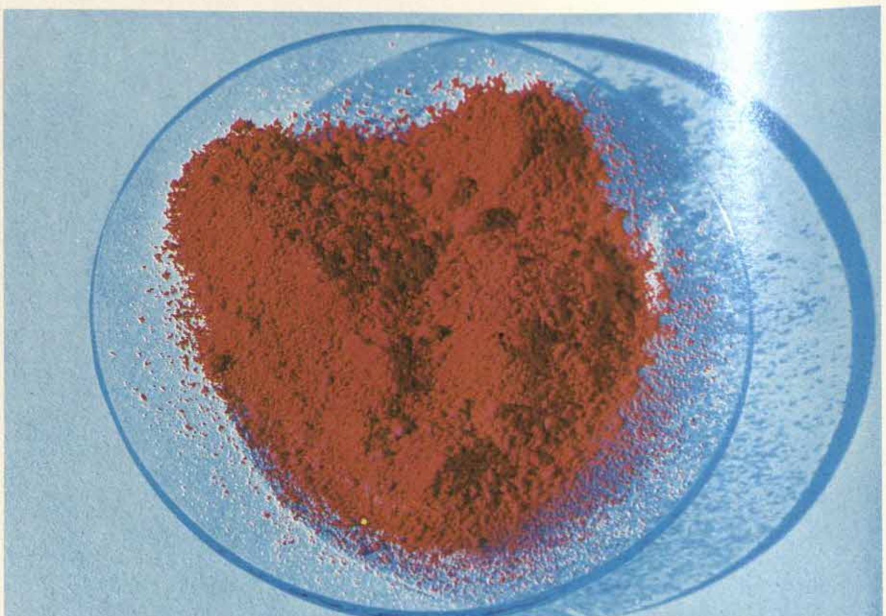
Metal-organic compounds of mercury are prepared by replacing the hydrogen in a C-H bond with the metal. Organomercury salts are extremely toxic, although they are of great importance in research.

ENVIRONMENTAL DANGERS

In the early 1970s, with new stress being put on environmental pollution, much attention was given to the dangers of mercury. A New Mexican family was poisoned by pork from animals that were fed seed grain treated with a form of organic mercury that affects the brain. Mercury from treated seed grain was found also in relatively high amounts in game birds of Montana and Alberta, Canada; and mercury was detected in fish in North American waters that are contaminated by industrial wastes.

A MERCURY-ORGANIC COMPOUND—The addition of mercuric chloride to an ammonia solution produces the milky-white mercuric amido chloride.

MERCURIC SULFIDE—If precipitated in solution, this sulfide is a black compound. However, when sublimated in a vacuum, it appears as the red rhombohedral crystals seen here. The sulfide is used to produce vermilion, a bright-red pigment, and is the only metallic sulfide that does not dissolve in nitric acid.



MOLYBDENUM AND TUNGSTEN | plant life and light bulbs

Molybdenum (Mo) and tungsten (W) are members, along with chromium, of the Group VIB series of elements. Both these metals bear strong resemblance to one another chemically and metallurgically, and each is present in the Earth's crust in amounts approaching 10^{-4} percent.

Molybdenum was known to the ancients, although it was confused with graphite and lead ore, galena. In fact, the name of this element is derived from the Greek *molybdos*, meaning "lead." Indeed, Aristotle appears to have made no distinction between lead ores and molybdenum.

In 1778 the Swedish chemist Carl Scheele showed that this metal's primary ore, molybdenite, was a distinct ore of a new element. In 1782 the Swedish mineralogist Peter Hjelm produced the first sample of the metal, although in an impure form.

A year after molybdenum was first prepared, metallic tungsten was produced following the reduction of tungstic acid with charcoal. This achievement, however, was based on considerable previous research. In 1779 it was concluded that a mineral now called wolframite contained an unknown substance. Then, in 1781, Scheele found that he could prepare a new acid from the mineral called tungsten (now known as scheelite). He and a co-worker postulated that a new metal could be obtained by reducing this acid. The production of metallic tungsten led them to the discovery that Scheele's acid was identical to one formed from wolframite, and their isolation of tungsten soon followed.

The name tungsten is derived from the Swedish *tung sten* (heavy stone), while its chemical symbol, W, comes from wolfram, an occasionally used synonym.

THE ELEMENTS AND THEIR MINERALS

While it does not occur as the free metal in nature, molybdenum is produced from its sulfide, molybdenite, MoS_2, and a lead-molybdenum mineral called wulfenite, $PbMoO_4$. Additionally, the metal can be obtained from other molybdates, such as that of magnesium, $MgMoO_4$. Molybdenum ores are mined in the United States, Canada, and parts of Asia and Europe.

To be commercially profitable, the relatively small amounts of molybdenum sulfide contained in the primary mineral must be concentrated. This is accomplished through a flotation process, with the product then converted to the trioxide by roasting. This impure form of the oxide is further clarified by dissolution in aqueous ammonia, and the resulting ammonium molybdate, $(NH_4)_2MoO_4$, undergoes further roasting to form pure trioxide. The oxide is finally reduced to the metal with hydrogen. (Reduction with carbon is undesirable because of carbide formation.)

Tungsten is found in nature almost exclusively in the form of tungstates (anionic WO_4^{3-} salts). The most important of these is wolframite, an isomorphic mixture of iron and manganese tungstates with the general formula $(Fe,Mn)WO_4$. Secondary minerals include scheelite, $CaWO_4$, huebnerite, $MnWO_4$, and ferberite, $FeWO_4$. The most important tungsten deposits are found in the United States, the Soviet Union, and parts of Asia, Europe, and South America.

The production of metallic tungsten begins with mechanical and magnetic enrichment of the ores, the mixtures being subsequently fused with sodium hydroxide. The mass is then dissolved in water to produce a solution of sodium tungstate, and this is reacted with an acid to cause precipitation of an insoluble

MOLYBDENITE—Almost all the world's supply of molybdenum is extracted from this sulfide. The largest deposits of this mineral are found in the western United States, Central and South America, Canada, and parts of Europe. Molybdenite crystallizes in the hexagonal system, appearing in fine layers that are soft, flexible, and gray in color.

oxide commonly called tungstic acid, H_2WO_4. With hydrogen, the dried oxide is finally reduced, at elevated temperatures, to metallic tungsten.

Both molybdenum and tungsten are true metals, having a shiny to white luster; in the pure form both are malleable and ductile. The latter properties are lost in the impure state. Electrically, molybdenum and tungsten are about one third as conductive as silver. Melting points of these metals are quite high: about 2,610° C (4,370° F) for molybdenum and 3,410° C (6,170° F) for tungsten.

APPLICATIONS

Both molybdenum and tungsten are valuable alloying agents, imparting special properties to steels. For example, molybdenum in amounts up to about one percent has a considerable positive effect on the hardenability and toughness of tempered steel. Certain tungsten-steel alloys have special application in high-speed cutting and milling equipment where ordinary metals would become soft and unusable.

Normal carbon steels may become extremely hard when tempered, but tend to lose this desirable property at elevated temperatures. While this can be overcome, an increase in the hardness of such steels leads to a decrease in resilience—the capacity to withstand mechanical shock without breaking. To retain hardness and resiliency, varying quantities of molybdenum, tungsten, chromium, and vanadium are alloyed with the steel. These elements combine with the carbon to form very hard carbides that are dispersed throughout the ferrous matrix.

In addition to their applications in the steel industry, molybdenum and tungsten are ideally suited to electronics. Because of their high melting points, both are used to make filaments for vacuum tubes and light bulbs.

Tungsten provides an excellent x-ray target, and both tungsten and molybdenum are being employed in the developing nuclear industries. Their strength and resistance to stress make them valuable materials in the aerospace fields. Molybdenum is also used to make certain nickel-based alloys resistant to corrosion.

FERROMOLYBDITE—This mineral is a product of the alteration of molybdenite and is found in compact masses or fibrous-radiated aggregates.

WULFENITE—This colorful mineral is a lead molybdate produced by the oxidation of the lead ores with which the primary metal is often associated.

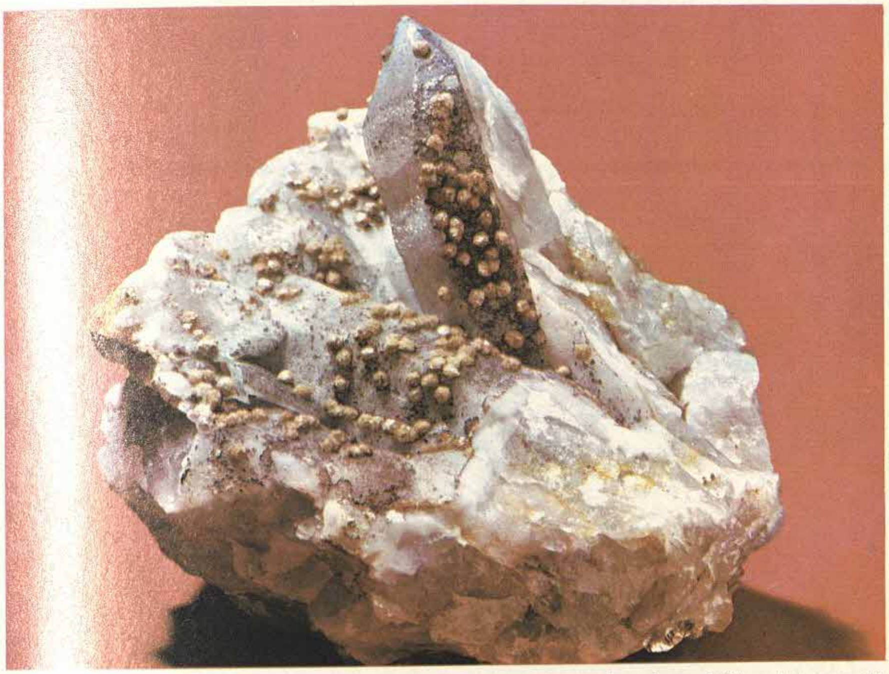
CHEMISTRY

Both molybdenum and tungsten resist attack by normal reagents, though both are dissolved by a concentrated mixture of nitric and hydrofluoric acids. Similarly, while not affected by the common alkalis, a fused mixture of potassium nitrate and sodium hydroxide will dissolve the metals rapidly.

Neither metal reacts with the atmosphere at room temperatures, but at red heat either combines with oxygen to form the trioxides. Their chlorides are formed by direct synthesis at elevated temperatures, while both react with fluorine under normal conditions to form the respective hexafluorides.

Although molybdenum and tungsten are both homologues of chromium, they do not exhibit totally similar properties. For example, the most stable ion of chromium is the trivalent, while stability for molybdenum and tungsten is achieved in the +6 state.

These two metals are responsible



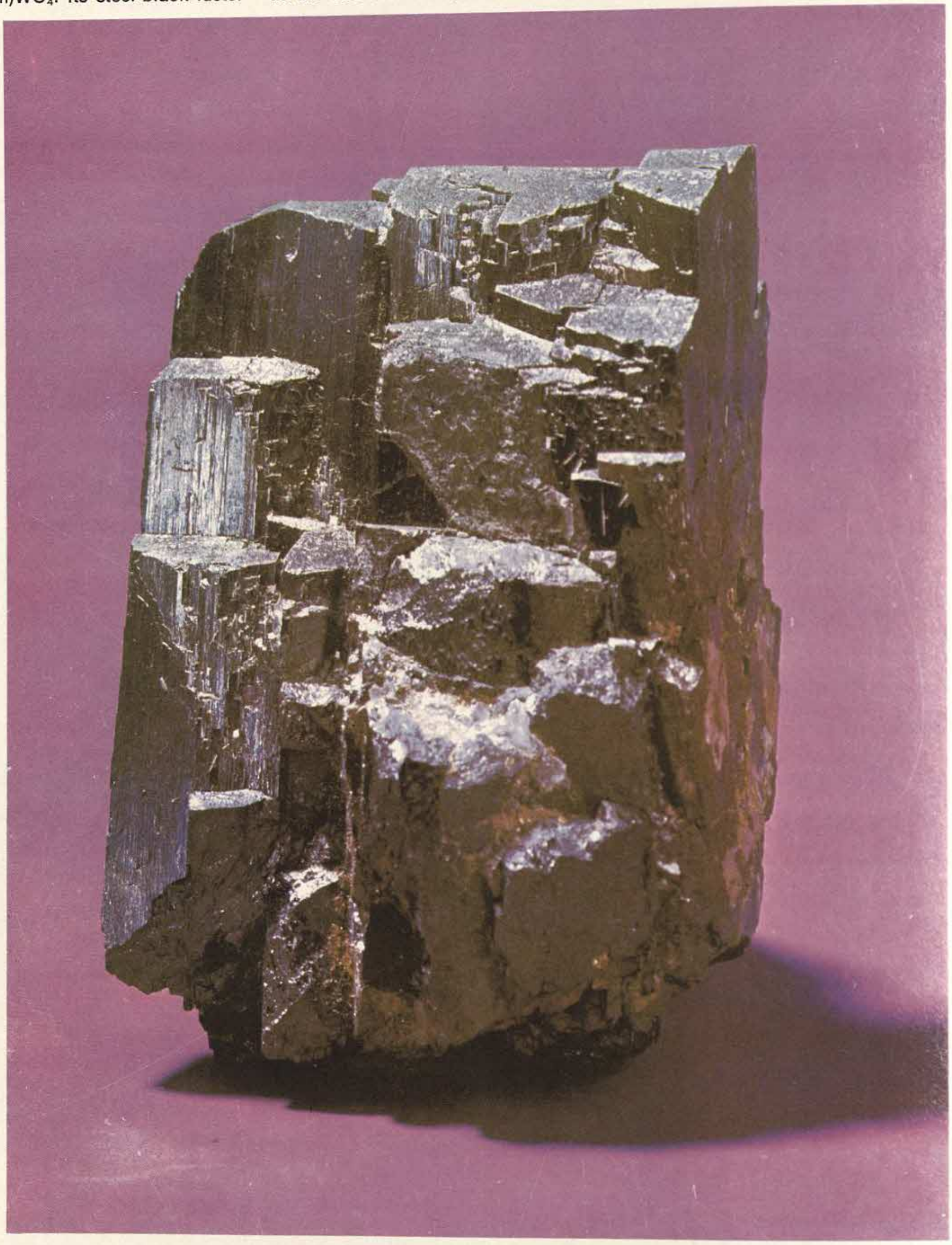
SCHEELITE (TUNGSTITE)—The nodules shown in the illustration are calcium tungstate, $CaWO_4$. Varying in color from yellow to brown, this tungsten mineral crystallizes tetragonally. The most important deposits are found in England, Finland, and Bolivia.

TUNGSTEN CARBIDE—This photomicrograph shows the structure of the extremely hard tungsten carbide. This material has been synthesized by a metal-ceramic process in which very finely divided tungsten carbide is fused with an alloy dust (cobalt, for example).

STOLZITE—Crystallizing in the tetragonal system, stolzite (lead tungstate) is a somewhat rare mineral. It is isomorphous with wulfenite, the molybdate of lead.

"RAPID STEEL" WITH TUNGSTEN AND MOLYBDENUM—Steels of the type illustrated in this photomicrograph are used to make tools that can withstand the high speeds of modern automated machinery. The "rapid steel" shown here contains 6 percent each of tungsten and molybdenum, and 4 percent chromium.

WOLFRAMITE—The specimen shown here is a mixed wolframite of iron and manganese with the formula $(Fe,Mn)WO_4$. Its steel-black luster highlights the monoclinic crystals commonly displayed by this mineral. Large crystals, such as the one illustrated, are often found in California and Germany. The largest deposits of this mineral are located in the western United States, southern Portugal, and China.



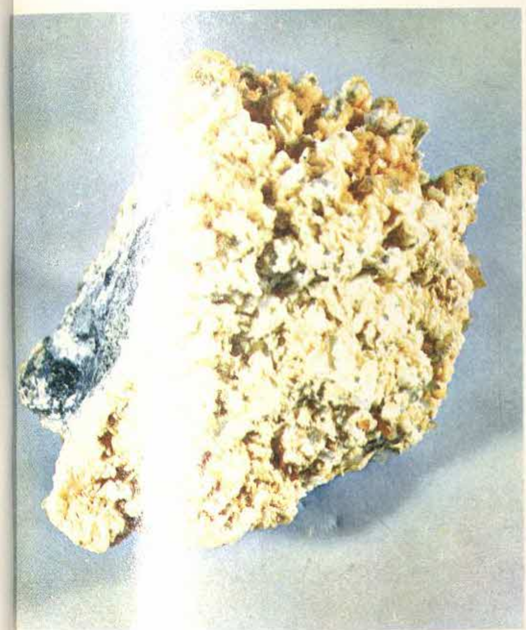
for a large number of oxides, and for an interesting series of nonstoichiometric oxyhydrates. One such compound is tungsten bronze, a chemically inert substance formed by the reduction of sodium tungstate with hydrogen and heat. These bronzes have the general formula Na_nWO_3, where n is greater than zero but less than one. As the value of n decreases, the color of the compound changes from bronze yellow to violet blue.

The most important molybdenum and tungsten compounds are the molybdates and tungstates, a series of salts built around the MoO_4^{2-} and WO_4^{2-} ions, in which the oxidation state of the metals is +6. On acidification, these anions polymerize to yield a complex series of polyanions.

In their stable hexavalent form, both metals combine with sugars and other organic compounds. In this respect, molybdenum is of particular interest to agriculture. In trace amounts, this metal is essential to proper plant growth, although the mechanism is not yet fully understood. It is known, however, that molybdenum is present in nitrogen-fixing bacteria.

MAGNESIUM | missiles, medicine, and photography

Although metallic magnesium (Mg) was not produced until the early part of the nineteenth century, some of its compounds had been discovered much earlier. For example, in 1695, an English botanist, Nehemiah Grew, became intrigued by the medicinal properties of the mineral waters at Epsom, England. His research led to the discovery of a



DOLOMITE—This double carbonate of magnesium and calcium crystallizes trigonally. The sample illustrated has its crystals joined to one another in saddle-shaped groups. Another form of the mineral consists of compact microgranular masses.

salt, which he appropriately named "Epsom salt," that was apparently responsible for the "curative" value of the spa. Subsequently it was found that Epsom salt was the sulfate of an unknown metal, magnesium.

In 1808 the English chemist Humphry Davy isolated magnesium after heating dry magnesium chloride with metallic potassium. In 1831 a reasonable quantity of the metal was produced.

Magnesium is a relatively reactive metal, and so is not found in the free state in nature. It is the eighth most abundant element in the earth's crust, and occurs primarily as the carbonate mineral magnesite ($MgCO_3$) and the mixed carbonate, dolomite, $MgCa(CO_3)_2$. Other magnesium minerals include chlorides, sulfates, and silicates. Of the last group, amianthus, an asbestos mineral, has an interesting history. Certain ancient civilizations exploited its nonflammability to make a cloth in which the dead were wrapped prior to cremation, thus creating an urn of sorts to contain the ashes. The nonflammable property of magnesium is used today to make nonburning upholstery, refractory liners, and incombustible paper.

Deposits of magnesium minerals are widespread, while seawater contains an abundance of soluble magnesium chlorides and sulfates. The Dead Sea, for example, contains an estimated 10 percent magnesium chloride and is a potentially rich source of the metal.

Botanically, magnesium is an important plant constituent because it is the central atom in chlorophyll, which is the catalyst in the synthesis of sugars from carbon dioxide and water during photosynthesis. The structural group in chlorophyll is but a step removed from the structure of the heme group in hemoglobin, the red pigment in vertebrate blood. The essential difference between chlorophyll and hemoglobin is the central atom: the former contains magnesium and the latter iron.

PREPARATION OF ELEMENTARY MAGNESIUM

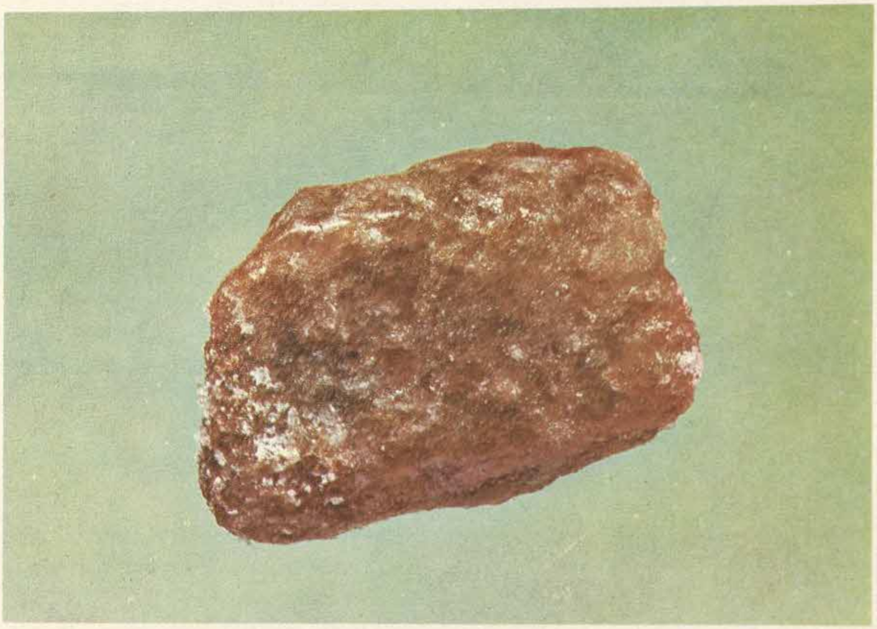
Almost all magnesium produced today is obtained by electrolysis of fused magnesium chloride, a compound derived from brine wells and seawater. The simple electrolytic reaction is carried out with a carbon anode and an iron cathode.

PROPERTIES

Elementary magnesium is a soft, silvery-white metal with a low specific gravity. In the air, it soon forms a protective surface coating of basic carbonate that prevents further oxidation. Like the other members of the Group IIA elements, its characteristic valence is +2.

KAINITE STRATA—Kainite is a monoclinic, prismatic mineral with the formula $MgSO_4 \cdot KCl \cdot 6H_2O$. It is found deposited in granular masses between potassium salts. Abundant deposits occur in Germany. In potassium deposits, the mineral is formed by metamorphism or the circulation of water.

CARNALLITE—This mineral is composed of magnesium chloride, potassium chloride, and water. It crystallizes rhombically as distinct crystals, but more often as compact microcrystalline masses that may be colored by impurities, as in this specimen. In the pure state, the mineral is white.



AMIANTHUS—Two variations of this mineral occur, the serpentine type and the hornblende type. The sample illustrated is the former, and is one of the asbestos minerals. Its formula is $Mg[(OH)_2Si_4O_{10}]$. The fibrous filaments are pliable and have a woolly texture.

Because it is extremely electropositive, magnesium reacts with hot water to produce hydrogen. This reaction is considerably less vigorous in cold water. When amalgamated with mercury, however, magnesium readily decomposes both hot and cold water.

In a normal oxygen atmosphere, metallic magnesium burns with blinding light and intense heat, forming both the oxide and nitride (Mg_3N_2). The violence with which it burns classifies it as a material to be handled with caution. Nevertheless, with its combustion controlled, magnesium's intense light is used in artificial light photography and in pyrotechnics.

Magnesium is readily soluble in all common acids, although it resists dissolution in cold alkaline solutions, probably due to the formation of protective oxides.

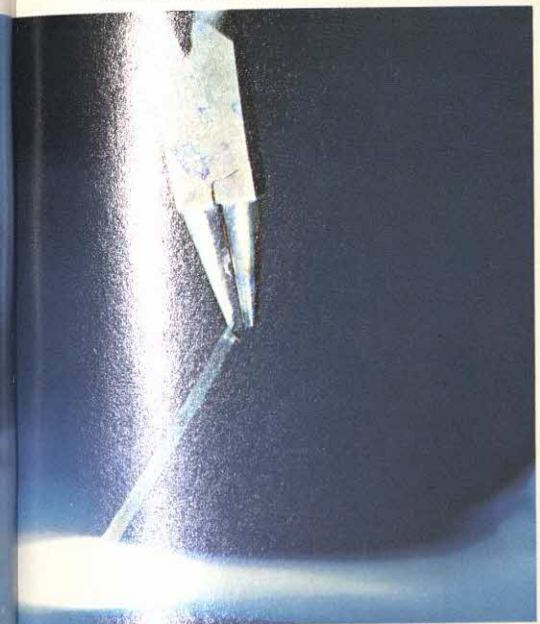
Perhaps the most important use of magnesium stems from its light weight and the properties it imparts to alloys. In itself, the metal has mediocre mechanical qualities but is able to improve these same qualities in other metals, notably aluminum, zinc, and manganese. The mechanical resistance of aluminum is improved, zinc is made more workable, and the corrosion of manganese is reduced—all by alloying these metals with magnesium. Such lightweight alloys have proved invaluable in the aerospace industries.

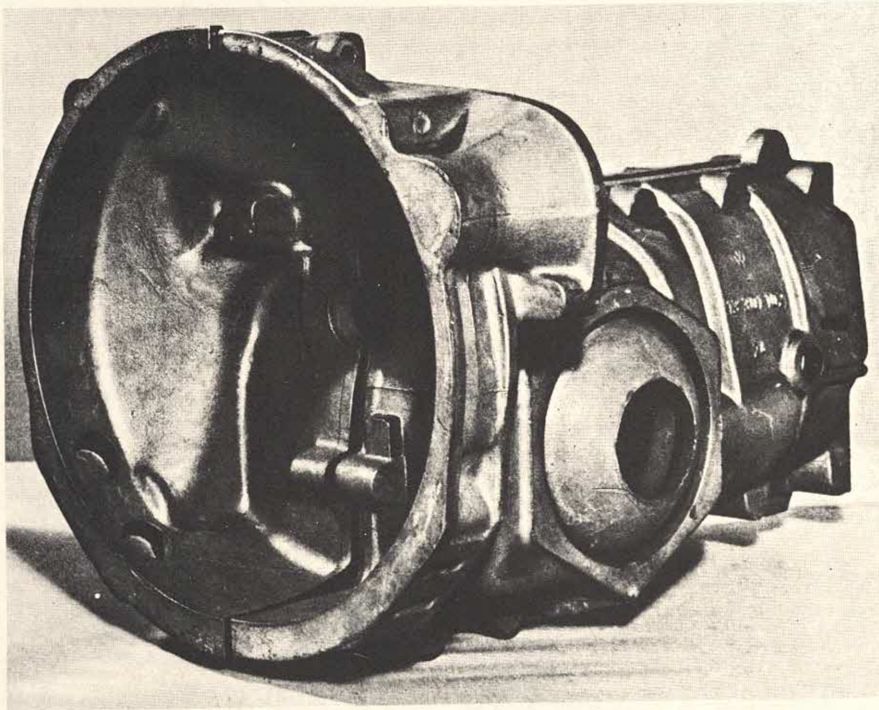
Sometimes used as alloying ingredients for special purposes are cerium, calcium, zirconium, cadmium, silver, silicon, beryllium, lithium, thorium, and tin. After World War I, intensive research and development work produced strong, light alloys. The rapid worldwide development of the aircraft industry greatly advanced the use of magnesium alloys for structural purposes. The perfecting of alloys that could be fabricated successfully by casting, extruding, rolling, and forging opened up many new fields of use. Special properties of magnesium make it particularly desirable where exceptional machining qualities and good fatigue resistance are important. Attainment of high standards in pressure die-casting technique has presented new spheres of application in the instrument, optical, and other industries where designers are often able to substitute a single casting for parts that were formerly built up from sheet and sections; the die casting is stronger and more rigid, but not heavier.

The greatest use of magnesium in aircraft was during and after World War II, when piloted aircraft were in extensive military use. Castings were employed in aircraft engine parts including crankcases, valve covers, superchargers, oil filters, and pumps. Landing wheels cast in magnesium were also used widely. Extrusions were used for floor beams, and magnesium sheet was used for the skin, for wing and control surfaces, and for the fuselage of airplanes and helicopters. With the phasing out of piloted aircraft and the advent of missiles, drones, and satellites, the tonnage of magnesium used in aircraft dropped considerably, but its usage became more versatile.

Magnesium alloys are used extensively in electronic structures. Magnesium is the choice for radar plotting consoles, antennas, power-supply cases, tape reels, memory disks, walkie-talkies, and chassis of various kinds. The light weight of magnesium alloys makes them highly acceptable to the tooling industry; to the materials handling industry, in which much of the equipment must be handled manually; and to makers of industrial high-

COMBUSTION OF METALLIC MAGNESIUM





MAGNESIUM ALLOYS—Magnesium alloys are used in many industries from the automotive to aerospace. Because of their light weight and excellent machining properties, such alloys are used to make housings for electric motors, typewriters, and optical instruments. The key to the use of magnesium alloys in missile technology is their mechanical resistance at high temperatures. In the illustration, the automotive clutch-differential-gear casing is a cast magnesium alloy.

speed and reciprocating machinery.

In the second half of the twentieth century the use of magnesium in consumer goods of many different types expanded constantly. It was used in the manufacture of luggage, cameras, lawn mowers, vacuum cleaners, and other electrical appliances. Magnesium was used also in sporting goods and office equipment.

MAGNESIUM COMPOUNDS

Magnesium oxide, MgO, can be obtained by heating the carbonate to red heat in special crucibles. At red heat, the oxide is white and soft. At increased temperatures, however, the material is converted to a heavier, more compact substance called dead-burned magnesite. With a melting point of 2,800° C (5,072° F), this compound is a very poor conductor of heat, making it suitable as a refractory liner.

Dissolution of the oxide in hot water yields the hydroxide $Mg(OH)_2$, better known as milk of magnesia, a common laxative. More important, however, is the hydroxide's role as the raw material for production of metallic magnesium. Extracted from seawater, the hydroxide is precipitated with lime and transformed into the chloride. Electrolysis yields the element.

Not only is magnesium chloride important as an intermediate in magnesium production; in the manufacture of cements it can be combined with magnesium oxide to form a hard and durable product. Sawdust added to this mixture forms a product called lignolite, used in the building trades for walls and floors. Portland cement is prepared, in part, of an equal mixture of magnesium chloride and oxide.

Magnesium sulfate, $MgSO_4$, (Grew's Epsom salts), is obtained by the evaporation of mineral waters. In aqueous solution the sulfate forms various hydrates, the more common containing one and seven molecules of water ($MgSO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$). The second form is used in medicine and in the textile industry as a weighting for silk.

Magnesite and dolomite are natural forms of magnesium carbonate, $MgCO_3$. Dolomite also contains calcium carbonate, which can be recovered by calcination and saturation with carbon dioxide in an aqueous solution. The magnesium carbonate dissolves before the calcium carbonate to form the bicarbonate $Mg(HCO_3)_2$, which is then isolated.

Finally, two magnesium salts, a silicate and the peroxide, are noteworthy. Talc, widely used in cosmetic preparations, is the magnesium silicate with the formula $Mg_3(Si_2O_5)_2(OH)_2$, while the peroxide, MgO_2, has properties similar to hydrogen peroxide, and is used as a bleach.

ORGANO-METALLIC MAGNESIUM COMPOUNDS

Some of the most important organic compounds contain magnesium, and these are called Grignard reagents. These compounds have the general formula RMgX, where R is an organic group (CH_3-CH_2-CH_2-, for example) and X is a halogen. The Grignard reagents form the basis for preparing a large number of organic compounds from which aldehydes, amines, and alcohols are obtained.

ANTIMONY | alloys, medicine, and makeup

The metallic element antimony (Sb) is neither widespread nor common in nature. Nonetheless, its history dates back to its use by the ancients, who recognized antimony in its compounds. The metal itself was not isolated until the beginning of the seventeenth century.

The early use of antimony compounds is described in the Bible through reference to "stibium," an eye cosmetic used by Egyptian women. The same source mentions various medicinal properties of stibium. From this Latin word antimony's chemical symbol, Sb, is derived.

Stibnite, the most important mineral of antimony, was recognized by the Greeks also as an eye cosmetic. Not until sometime around the first millennium A.D., however, did the term *antimonium* come into use. It is from this Latin term that the name of the metal originates.

Metallic antimony was first prepared about 1615 by the German alchemist Libavius, following the treatment of stibnite (antimony sulfide) with iron. Today, this mineral continues to be the primary source of the element. Rich stibnite deposits occur in Asia and in Central and South America. Other mineral sources include the antimonides and sulfantimonides of the heavy metals, and the oxides.

Antimony is a member of the Group VA elements, along with nitrogen, phosphorus, arsenic, and bismuth. Its properties resemble both those of the less metallic arsenic and the more metallic bismuth.

1

THE DAUGHTERS OF AMENOPHIS IV—The Bible mentions stibium (stibnite, the most important mineral of antimony) as being used by Egyptian women as an eye cosmetic. The detail in the illustration is from a fresco in the tomb of Nebamon (eleventh century B.C.).

2

STIBNITE—This specimen of antimony trisulfide shows its rhombic crystalline formation.

PREPARATION OF METALLIC ANTIMONY

Elementary antimony is produced industrially by the roasting of the sulfide with subsequent conversion to the oxide and final reduction with iron, or by direct reduction of oxide ores with carbon:

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2$$
$$Sb_2O_3 + 2Fe \rightarrow 2Sb + Fe_2O_3$$
$$2Sb_2O_3 + 3C \rightarrow 4Sb + 3CO_2.$$

The metal prepared in either of these reactions is impure, and electrolysis is employed to produce antimony exceeding 99.999+ percent purity.

There are four allotropes of antimony: yellow, black, explosive, and metallic (ordinary). The first two modifications are stable only at low temperatures; yellow antimony occurs only below −40° C (−40° F). At this point, the black allotrope is formed. Neither can be characterized as a true metal. Explosive antimony can be prepared by electrolysis of the chloride, and when heated it will explode to become the common form of the element. It has been shown that explosive antimony is amorphous, and that it contains traces of the chloride. Explosion occurs when amorphous antimony changes to a stable crystalline form that releases 19,600 calories of heat per gram.

Metallic antimony is very stable but extremely brittle, with a flaky, crystalline structure. To some extent it resembles silver in luster and lead in color. The metal is not altered by exposure to the atmosphere at normal temperatures, although when heated it burns intensely with concurrent evolution of white antimony oxide fumes. Thermally and electrically, antimony is classed among the poor conductors. The stability of the metal is further exemplified by its resist-

3

PYRARGYRITE—The gray mineral (Ag_3SbS_3) is a thioantimonite of silver, and is shown here in association with calcite. Like stibnite, pyrargyrite crystallizes rhombohedrically.

4

BOULANGERITE — This magnificent monoclinic crystal is a double sulfide of antimony and lead. The specimen illustrated was found in Sweden.

5

METALLIC ANTIMONY—Common antimony, as seen here, is one of four allotropic forms of the element, and by far the most stable. Its color and luster belie a fragile crystalline structure.

6

TARTAR EMETIC—Though used in medicine, tartar emetic or potassium antimonyl tartrate is more commonly used as a mordant in the textile industry.

ance to attack by most common reagents; it is soluble only in hot concentrated acids (especially sulfuric) and aqua regia.

The compounds of antimony are similar to those of arsenic and, though less toxic, are still extremely poisonous. In the formation of its compounds, antimony demonstrates stable oxidation states of +3 and +5, though certain compounds illustrate a −3 valence. As elementary metal, antimony is used primarily in alloying, notably with lead and tin. It greatly increases the durability of lead, thus lending such alloys importance in the manufacture of automotive storage batteries and in the production of bullets. Additionally, low or antifriction alloys contain the metal, and its low melting point makes it a valuable material in the manufacture of fuses and other safety devices. Antimony compounds are also used as pigments in paint and rubber, and in the ceramics industry.

COMPOUNDS OF +3 ANTIMONY

Antimony trioxide, being insoluble in water, occurs in nature as the mineral senarmontite, and is also the product of the burning of the metal in air. While the compound is generally seen in a molecular structure expressed as Sb_2O_3, it may take on the form represented as Sb_4O_6. This compound behaves amphoterically depending on its environment, resulting in acidic or basic solutions. In alkaline solution, +3 antimony compounds are energetic reducing agents.

In the laboratory, antimony trisulfide (Sb_2S_3) is a product of the reaction between hydrogen sulfide and antimony trichloride. The compound, when first formed, has a fine red-orange color, although this changes in time to a gray-black corresponding to stibnite, or natural antimony trisulfide. In alkaline solutions of sodium sulfide, the trisulfide dissolves readily to yield thioantimonite, SbS_3^{3-}.

Antimony combines with all the halogens, forming products of the general type SbX_3 in the trivalent state. The trichloride is not a salt in the true sense because of an inability to conduct electricity. This property makes it useful in the protection of some metals from corrosion. The trichloride is also used to burnish alloys such as brass or metals such as iron. In such circumstances, the surface of the base metal goes into solution with the chloride and a fine deposit of protective antimony remains. Antimony trifluoride, unlike its chlorinated cousin, is a salt in every sense.

Antimony hydride or stilbene (SbH_3) is a highly toxic gas resembling arsine. The gas can be condensed to a white solid, and if the solid is heated it demonstrates a lesser affinity for hydrogen than arsenic: the compound readily decomposes.

COMPOUNDS OF +5 ANTIMONY

Dissolving elemental antimony in hot, concentrated nitric acid yields the pentoxide Sb_2O_5. This oxide is only slightly soluble in water, but that which does dissolve gives a weakly acidic reaction. In contrast, the arsenic and phosphorus oxides are very reactive to water and yield moderately strong acids.

In concentrated nitric acid, antimony pentoxide forms antimonic acid with the formula $HSbO_3 \cdot 3H_2O$. The potassium salt of this acid demonstrates a greater solubility product than the corresponding sodium salt.

The pentahalogen series of antimony corresponds with its trihalogens. The pentachloride, $SbCl_5$, is prepared by direct synthesis of the trichloride and elementary chlorine, but this compound is quite unstable; the reaction is easily reversible. This property makes the pentachloride a useful source of chlorine. In aqueous solution the pentachloride hydrolyzes, unlike the pentafluoride, which is stable in water. However, the latter will react in water to yield the interesting compound $(SbF_5OH)^- \cdot H_3O^+$.

Antimony's pentasulfide, Sb_2S_5, is readily soluble in the common alkali solutions; the resultant products are the thio salts. The most important of these is Schlippe's salt, used to prepare a highly reactive sulfide important in the vulcanization of rubber.

As to antimony's therapeutic uses, the compound known as tartar emetic, or potassium antimonyl tartrate, causes immediate vomiting, rapidly cleansing the stomach of poisons. Nevertheless, antimony and its compounds seldom are used as therapeutic agents because of harmful side effects and because other less dangerous agents are available for medical application.

7

STEPHANITE—Another sulfide of silver and antimony, this mineral is abundant in Mexico and Colorado.

TETRAHEDRITE AND DYSCRASITE—The beautifully formed crystals in Illustration 8a are tetrahedrite, a sulfide of copper and antimony that always occurs in combination with other sulfides. The silver antimonide in Illustration 8b is the mineral dyscrasite.

8a

8b

RHODIUM, IRIDIUM, AND PALLADIUM | three noble metals

Each of these members of the platinum group of metals was discovered at the beginning of the nineteenth century, rhodium (Rh) and palladium (Pd) by the English chemist and physicist William Wollaston and iridium (Ir) by the English chemist Smithson Tennant. Because these elements exhibit very similar chemistries, their isolation from one another was one of the more difficult aspects of their discovery.

The name "rhodium" is derived from the Greek *rhodon,* meaning "rose," the color observed in hydrated chlorides of the element by Wollaston. Metallic rhodium is a silvery-white substance with a very high melting point—about 1,966° C (3,750° F). At red heat, the metal changes to the sesquioxide in air, but further heating causes the oxide to reconvert to the metal. The low electrical resistance of rhodium and its excellent resistance to corrosion make it an ideal material for use in electrical contacts. Alloys of platinum and rhodium are extremely hard, and are used to make bushings utilized in the production of glass fibers and in other processes where resistance to abrasion is critical. Rhodium in colloidal suspension has strong germicidal properties.

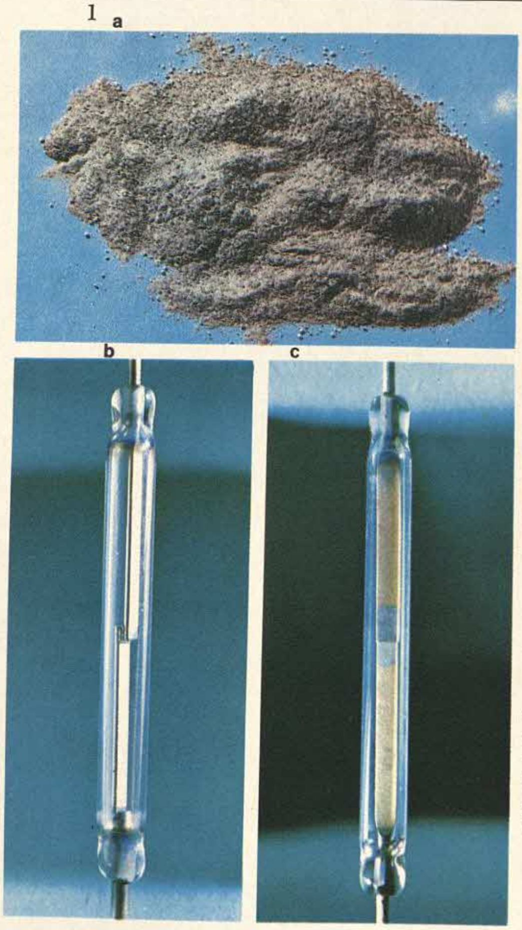
Iridium is an extremely hard, brittle metal that takes its name from the many-colored hues—the iridescence—of its salts. This is the most corrosion-resistant metal known, and as such is part of the alloy composing the standard meter, a metal bar, housed in Paris, that represents the international unit of length. Iridium is used primarily as a hardening agent in platinum alloys. These alloys are used for jewelry and surgical pins and pivots. With their superior resistance to the action of the high-temperature electric spark, they are widely used for electrical contacts and sparking points. Iridium is also used in special laboratory crucibles for high-temperature analysis, and it is used in osmium alloys for fountain pen points.

Iridium and osmium are presently the subjects of scientific debate concerning which of the two is the densest metal. When this debate is resolved, one will have the distinction of being the heaviest natural element.

Palladium was named for the asteroid Pallas, discovered two years prior to the discovery of palladium. It is the least dense and lowest-melting of all the platinum metals, and has the unique ability to absorb 900 times its volume of hydrogen at room temperature. When heated, palladium allows hydrogen to diffuse through it, and thus can be applied as a purifier for the gas. In the finely divided state, the metal is an excellent catalyst for hydrogenation and dehydrogenation reactions. Like gold, palladium can be beaten to extreme thinness—in fact, into sheets only 1/250,000 in. thick. This malleability lends the metal applications in fashioning jewelry; with gold, palladium forms the alloy known as white gold. Because it can be cold-worked, and because it is highly resistant to corrosion, palladium is used in dentistry and for making surgical instruments.

Each of these three noble metals forms a respectable number of compounds, and in so doing demonstrates oxidation states of +3 for rhodium, +3 and +4 for iridium, and +2 and +4 for palladium.

1 a b c



CHEMISTRY OF RHODIUM—Pure rhodium is obtained by the reduction of pentammine-rhodium chloride, $Rh(NH_3)_5Cl_3$. In the compact form the metal is unaffected by the common acids or aqua regia; when finely divided, however, the opposite is true. The pure metal is used to electroplate silver, protecting the base metal without altering its appearance.

Rhodium's most stable oxidation state is +3, and such compounds include the oxide and hydroxide, the sulfide, and the halides. The oxide, Rh_2O_3, is easily obtained by heating the metal in air. Compared to the oxides of the other platinum metals, rhodium oxide is an extremely stable compound, decomposing at temperatures only above 1,000° C (1,832° F).

Rhodium hydroxide, $Rh(OH)_3 \cdot H_2O$, is an amphoteric compound, reacting as an acid or a base depending on its environment. The sulfide, Rh_2S_3, can be prepared by direct synthesis of the elements or by reacting solutions of rhodium and sulfur salts.

While rhodium forms compounds with all the halogens, its bromide and iodide compounds are fairly unstable. Both the chloride and fluoride are red compounds prepared by direct synthesis, and both exhibit a reasonable degree of stability.

Illustration 1a shows rhodium dust; Illustrations 1b and 1c show practical applications of the metal. In the former, a small rhodium plate has been soldered to silver contacts on the electrical relay. The latter illustration shows a relay with gold-covered contacts onto which rhodium has been electrolytically deposited.

2

CHEMISTRY OF IRIDIUM—The powdery gray mass shown is finely divided iridium. Electronically, this element's most stable valences are +3 and +4, although the metal exhibits zero and +1 oxidation states in certain compounds.

When reacted with chlorine at temperatures between 600 and 700° C (1,112 and 1,292° F), finely divided iridium forms the trichloride, $IrCl_3$. The compound is a green, powdery material that is insoluble in water.

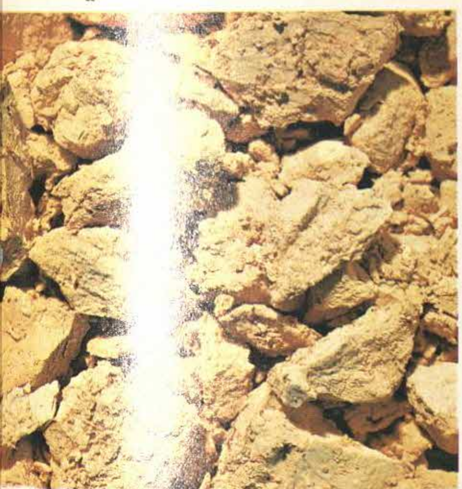
Iridium hydroxide, $Ir(OH)_3$, is a rather unstable substance that tends to combine with oxygen, forming the more stable dioxide. This reaction demonstrates iridium's most stable oxidation state, +4. The dioxide, IrO_2, is highly unsoluble in water, and is not affected by any of the acids, even when the acid is heated.

Although iridium does form halides in its +4 state, these compounds are not very stable.

3

CHEMISTRY OF PALLADIUM—Palladium is the most important of the platinum metals. Because of the ease with which it absorbs hydrogen when the metal is finely divided, palladium is used in numerous catalytic reactions. The main source of the metal is the nickel industry, where palladium is obtained as a by-product.

a



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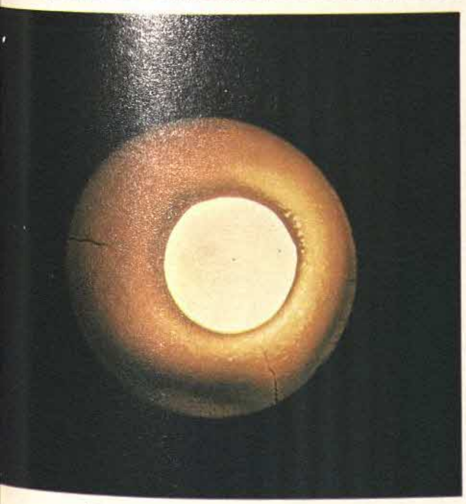


c

d

Like platinum, palladium is silvery-white, but when heated in the air loses its luster and becomes the oxide, PdO, a strong oxidant. Palladium is the softest and most ductile of the platinum metals.

It is in the production of special alloys that palladium finds its major use. Such alloys are used, for example, to make delicate, high-precision instruments such as surgical tools or bearings for analytical balances.

Illustration 3a shows ammonium chloroplatinate, which when heated forms the palladium "sponge" in Illustration 3b. When the "sponge" is melted (Illustration 3c), the result is the pure metal (Illustration 3d), ready for working into sheets or for alloying with other metals.

Finely divided palladium can be used to obtain hydrogen of extremely high purity, and such gas is important in precision physical research. The metal's best-known alloys are those used in ornamental work such as jewelry. White gold is an alloy of 80 percent gold and 20 percent palladium.

Palladium exhibits two oxidation states, +2 and +4; the former is the more stable. Of the bivalent compounds, the oxide is the most important, and it is obtained by reacting palladium chloride with alkalis. The chloride is important not only as a reactant in this process, but also as a detector of deadly carbon monoxide. In the presence of this gas, the chloride is reduced to hydrochloric acid, carbon dioxide, and black, metallic palladium. The color of the metal indicates the presence of the gas.

Palladium sulfide is obtainable by direct synthesis of the elements. The metal also forms relatively stable halides, notably the bromide and iodide.

In the +4 oxidation state, palladium compounds are somewhat difficult to produce and are relatively unstable. The dioxide, PdO_2, when hydrated with a water molecule, forms a red compound that easily loses an oxygen atom. The disulfide, obtained by direct synthesis, is black like palladium sulfide, but is less stable.

LITHIUM AND POTASSIUM | mental health and fertilizers

Lithium (Li) and potassium (K) are the first and third members of the alkali metals in Group IA of the periodic table of the elements. These two elements, along with sodium, are among the most reactive elements, and are never found in a free state in nature.

Having all of the properties generally associated with metals, lithium and potassium are good conductors of heat and electricity; in the pure state, they have a silvery luster and are quite soft. Both are extremely ductile and malleable, although they must be handled with extreme care because of their reactivity in air.

Lithium and potassium have the crystalline structure common to the other Group IA metals. Both are univalent, the valence electron creating a cloud of negative charge within the crystal lattice. This is one explanation of their plastic mechanical properties. Lithium and potassium can be cut with a knife because of the uniform charge distribution throughout their structures. The attractions (between the electrons and the nucleus) allow the metals to undergo considerable alteration with destruction of the electrical equilibrium. This is in sharp contrast to iron, for example, which is much harder and more brittle than the alkali metals, and which has a tendency to maintain its shape at normal temperatures.

The accompanying chart of the alkali metals shows that their properties vary uniformly with respect to increasing atomic weight. The ionization potentials and melting and boiling points show a constant decrease, while ionic radii and density (or specific gravity) increase proportionately. The relatively large differences between the properties of lithium and those of the elements following it are due to its small ionic radius.

Because the lone valence electron is weakly bound, the alkali metals readily produce brilliant emission spectra. Examples are provided when the easily volatilized chlorides are held in a flame, showing the characteristic colors for these elements: red for lithium, yellow for sodium, violet for potassium, and red and blue for rubidium and cesium, respectively. The common flame test for the presence of these elements is based on these emission spectra.

CHEMICAL PROPERTIES

Because they tend to lose their valence electrons easily, the alkali metals are strong reducing agents. The pure metals are unstable when exposed to air, and must be stored in mineral oil. They react violently with water, liberating hydrogen—a reaction that increases with atomic weight of the alkali metal used. The general equation for this reaction is $2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$. Rubidium and cesium, the largest of the alkali metals, are so reactive that they can only be handled in an inert atmosphere and are explosive in contact with moisture. Cesium, the first element discovered by use of the spectroscope, is the most reactive of all metals, melting and inflaming on exposure to air.

With oxygen, the alkali metals form several compounds: oxides (with the general formula M_2O); peroxides (M_2O_2); trioxides (M_2O_3); and superoxides (MO_2), although not all are formed by every element. The oxides react with water to produce hydroxides according to the reaction $M_2O + H_2O \rightarrow 2M^+ + 2OH^-$. On the other hand, the peroxides yield hydroxides and hydrogen peroxide:

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2.$$

The alkali metal hydroxides react with all common acids to produce salts. These compounds are solid, ionic, crystalline, and colorless, with high melting points. They are all soluble in water, and in the fused state are good electrical conductors.

PETALITE—Although lithium is widely distributed in nature, its concentration in ores is relatively low. The sample of petalite in the illustration has the composition $Li(AlSi_4O_{10})$. Other important lithium ores are spodumene and lepidolite.

1

SYLVITE (POTASSIUM CHLORIDE)—This ore crystallizes cubically and often contains sodium and magnesium chlorides as impurities. Similar in appearance to rock salt, it differs both in taste and in the color it imparts to a flame.

2

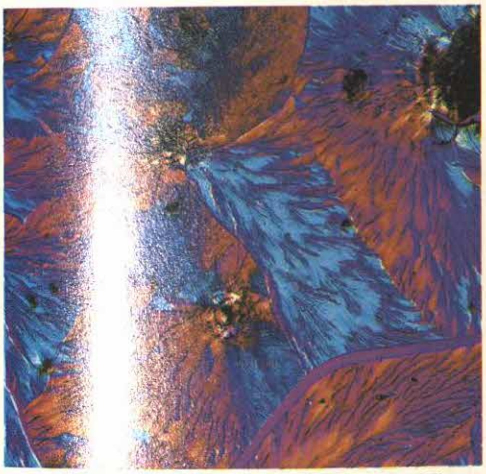
ORTHOCLASE (POTASSIUM FELDSPAR)—These orthoclase crystals are the amethyst variation of quartz. The composition of this mineral is $KAlSi_3O_8$.

3

4

PHILLIPSITE, $KCa(Al_3Si_5O_{16}) \cdot 6H_2O$—This potassium ore forms monoclinic crystals. It is just one of many occurrences of twin crystals in which two or more elements assume a rhombododecahedral structure.

5



IRON AND POTASSIUM SULFATES—These compounds, from aqueous solutions, were photographed under polarized light. (100 X)

NATURAL DISTRIBUTION, PRODUCTION METHODS, AND USES

Sodium and potassium are the most widely distributed alkali metals, occupying sixth and seventh place in abundance, respectively. Less widely found is lithium, while rubidium and cesium are quite rare. Francium, the last of the alkali metal group, exists only in the nuclear physics laboratory, where it has been identified through the decay of its nucleus. Since most of the compounds of these metals are soluble, they are found in seawater, in salt springs, and in some deposits formed by the evaporation of ancient seas. Combined with oxygen and silicon, they are also found in silicates, the largest group of minerals in the Earth's crust.

Ions of sodium and potassium are basic constituents of plant and animal tissue. Physiologically, sodium is of vital importance; it is part of the electrolyte system in the human body, and its absence or excess can be fatal. A common symptom of a loss of sodium is "summer weakness," caused by sweating. The simple salt tablet is an immediate remedy.

The alkali metals cannot be produced by direct chemical methods because no reducing agents are more powerful than the metals themselves. Thus, they are obtained by the electrolysis of their fused compounds. Electrolysis of their aqueous solutions is ineffective because hydrogen is evolved at the cathode. (Even hydrogen is reduced more readily than the alkalis.)

Industrially, the alkali metals are used as strong reducing agents in the preparation of soluble salts of many acids. In the molten state, the metals are used in nuclear reactors to transfer heat away from the core. One disadvantage of the molten alkali metals results from their vigorous attack on most materials.

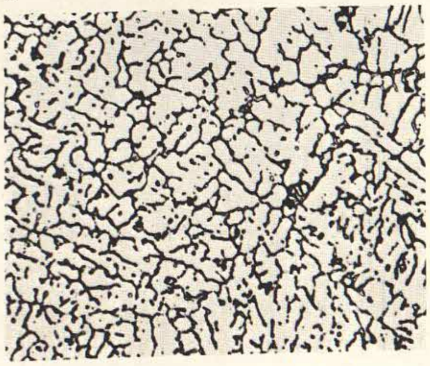
LITHIUM

Lithium, the lightest of all metals, with a density only half that of water, was discovered in 1817 by the Swedish chemist Johann-August Arfvedson. At the time of its discovery in one of its ores, petalite, it was believed to occur only in minerals. Hence, its name is derived from the Greek *lithos* meaning "stone." Later investigation showed its presence in the human organism and in plants, however.

The most important ores of lithium are lepidolite (also called lithium mica), spodumene, petalite, and amblygonite. In the pure state, lithium is less reactive than the other alkali metals. In solution, however, it is the strongest reducing agent known. Were it not for its extremely corrosive effect on other materials, it would find efficient use in heat exchangers due to its high specific heat (0.784 calories per gram at 0° C). In the metallic state, lithium has limited use, though a minute quantity was used to make the glass for the 200-in. Mount Palomar telescope. Lithium also finds some application in metallurgy to degas

ALUMINUM-COPPER-LITHIUM ALLOY—This is a photomicrograph of an alloy containing 87 percent aluminum, 10 percent copper, and 3 percent lithium. (100 X)

6



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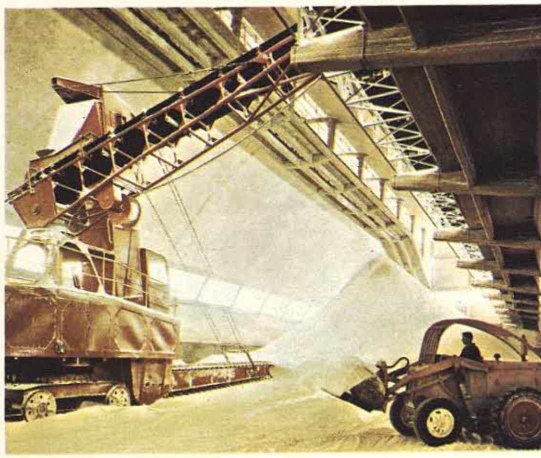

KAINITE—Large quantities of this potassium ore are used as a raw material in industry.

MICROSTRUCTURE OF THE ALUMINUM-COPPER-LITHIUM ALLOY—This photomicrograph of the alloy in Illustration 6 reveals the aluminum-copper-lithium mixture as dark areas. The lighter spaces are copper-aluminum mixtures with traces of iron impurities. (500 X)

8

Element	Atomic number	Ionization potential, ev	Ion radius, Å	Density, g/c^3	Melting point, °C	Boiling point, °C
lithium	3	5.39	0.60	0.53	179.0	1,317
sodium	11	5.14	0.95	0.97	97.5	883
potassium	19	4.34	1.33	0.86	62.3	760
rubidium	37	4.18	1.48	1.53	38.5	700
cesium	55	3.89	1.69	1.87	28.6	670
francium	87	–	(1.75)	–	–	–

copper and its alloys and to harden lead- and calcium-based alloys.

Among the compounds of lithium are lithium carbonate, recently found useful in the treatment of manic depressive psychosis, and the bicarbonate, used to combat hyperuricemia (excess uric acid in the blood). Aside from their medical uses, lithium compounds such as the fluoride are used in making special lenses for infrared spectroscopes. Lithium aluminum hydride is a reducing agent employed in organic chemistry. Lithium chloride is one of the most hygroscopic materials known, and is able to extract large quantities of moisture from the air. In this respect it is occasionally used in air conditioning and industrial drying systems.

POTASSIUM

The name potassium comes from the archaic term "pot ashes," used to describe the extraction of sodium nitrate by evaporation of its aqueous solution in an iron pot. The element was unknown to medieval alchemists, who confused sodium carbonate with potassium carbonate. The symbol of potassium, K, is derived from the Latin *kalium*. The element was discovered in 1807 by the English chemist Sir Humphry Davy, and was the first metal to be isolated by electrolysis.

Widely distributed in nature, the primary deposits of potassium are in the form of silicates such as leucite and orthoclase. By weight, potassium makes up about 2.4 percent of the Earth's crust, mostly in the form of insoluble compounds.

Secondary potassium deposits of the ores sylvite, carnallite, and kainite are also quite widespread. Sylvite and carnallite, for example, are found in ancient lake and seabeds, which provide a relatively accessible source of the element. It is also present in seawater, but only to a minor extent compared to sodium.

Having few advantages over sodium, metallic potassium finds little use in industry. In combination with sodium, however, it is used to make an alloy containing about 77 percent potassium. This alloy melts at −13.3° C (7.06° F) and is used as a coolant in nuclear reactors.

The most important potassium salts are chloride, nitrate, and sulfate; they are used mainly in fertilizers. In many chemical applications, potassium salts are preferable to those of sodium because of their better solubility and crystallization factors. In the glass and soap industries, potassium carbonate finds wide use, and potassium nitrate (saltpeter) is one of the major ingredients in black gunpowder.

OTHER USES OF POTASSIUM

Many salts and preparations of potassium are used in medicine. Potassium acetate has been recommended in the treatment of cardiac arrhythmias; potassium arsenite solution, for chronic myelogenous leukemia; and potassium bicarbonate, as an antacid.

Potassium bromide is used in medicine as a sedative, and it is used also in the preparation of photographic emulsions and in process engraving. Potassium iodide is used in organic chemical syntheses, in animal and poultry feed, and in table salt.

The most successful "decay clock" for dating archeological events so far is the potassium-argon method. It is based on a so-called closed system in the sense that radioactive potassium (with a half-life of 1,300,000,000 years) decays into argon, and both are locked in with the parent material that is being dated. The long half-life makes possible the dating of objects that are far too ancient to be accessible to the radiocarbon method of dating.

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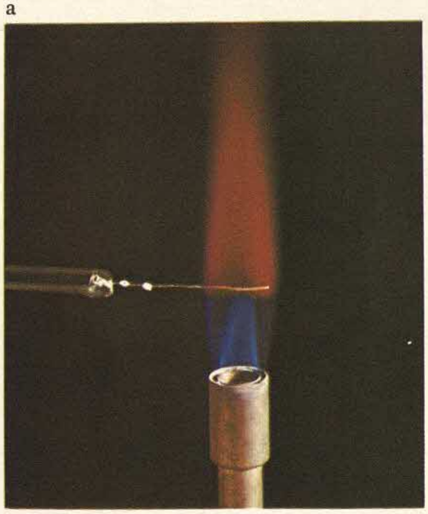

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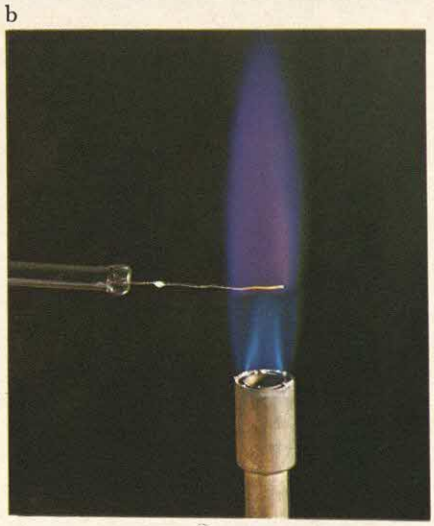


LITHIUM AND POTASSIUM FLAMES — When held in a flame, many salts volatize and produce characteristic colors. The red flame in Illustration 9a is typical of lithium compounds (the chloride is used because of its volatility), while the purple flame in Illustration 9b characterizes potassium compounds.

TITANIUM | from earthbound steels to outer space

HISTORICAL INFORMATION

Titanium (Ti), atomic number 22, along with zirconium and hafnium, is a member of Group IVB of the periodic table. The discovery of this element is generally attributed to the English mineralogist William Gregor. In 1791, while studying the black sands near the Cornish town of Manaccan, he found that some of the grains stuck to a magnetic mineral. Dissolving some of these grains in hydrochloric acid, he obtained a green, insoluble precipitate and a solution containing iron. Analysis of the precipitate revealed the presence of magnesium and silicon and some other substance whose nature was not fully understood. Gregor named this substance menachanite, after the town of Manaccan.

Four years later the German chemist M. H. Klaproth conducted independent research on the same minerals. His work convinced him that a new element had been discovered. He named this element titanium, from the Latin *Titans,* the first sons of the Earth in mythology. Titanium and its properties were finally studied and described by the Swedish chemist J. J. Berzelius (1825) and the German chemist Friedrich Wöhler (1849). Not until 1910, however, was the pure metal obtained.

TITANIUM—Two allotropes of this metal exist: the alpha form, a compact, hexagonal lattice, stable at ordinary temperatures; and the beta form, which occurs at temperatures above 882° C (about 1,620° F), and is unstable below this point.

ORES AND PROPERTIES

Titanium makes up 0.6 percent of the weight of the Earth's crust, and is the ninth most abundant element, exceeding chlorine, carbon, and sulfur in quantity. Although titanium is widely distributed, rich deposits of the element are rare. It is almost always present in igneous rock and its sediment; it is found in meteorites, and has been detected in the sun through spectroanalysis.

The major titanium ores are rutile, a tetragonal variety of titanium dioxide; ilmenite, or iron titanate; and sphene, a complex mineral containing calcium, silicon, oxygen, fluorine, hydrogen, and titanium.

Because it combines readily with carbon to form an extremely stable carbide, titanium cannot be obtained by ordinary carbon reduction processes. It also combines readily with oxygen, nitrogen, and hydrogen, all of which have an adverse effect on its mechanical properties. As a result, titanium must be processed in their absence.

In 1946, the Kroll process was invented to obtain the pure metal from its tetrachloride. An ore such as rutile is heated to red heat with carbon and chlorine to produce the tetrachloride: $TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$. The tetrachloride, a fuming, corrosive liquid with a melting point of −25° C (−13° F) and a boiling point of 136.4° C (about 277° F), is purified by fractional distillation. The liquid then is reduced to the metal with magnesium at 800° C (1,472° F) in an argon atmosphere. From this process, titanium emerges as a spongy mass that can be melted in an electric furnace (again in an inert atmosphere) and shaped into ingots.

Extremely pure titanium can be obtained on a laboratory scale by means of the van Arkel-deBoer process. Instead of the tetrachloride, titanium tetraiodide is vaporized in a vacuum, and the pure metal is deposited on an incandescent tungsten filament.

PHYSICAL AND MECHANICAL PROPERTIES

At normal temperatures, titanium atoms form a compact hexagonal lattice. This structure changes at around 882° C

RUTILE—This mineral is the most common allotropic form of titanium dioxide. The illustration shows a piece of quartz that contains interwoven, needle-shaped rutile crystals.

(about 1,620° F) to a cubic formation. In many ways, this element is similar to other transition metals such as iron and nickel; it is hard and refractory—it melts at 1,725° C (3,137° F) and boils at 3,262° C (about 5,903° F)—and is a good conductor of heat and electricity. Titanium has a low specific gravity compared to other metals that resemble it mechanically and physically. Because it is quite resistant to many types of corrosion and to high temperatures, titanium is used in turbines, in marine engineering, and in the chemical industry.

Although not too reactive at ordinary temperatures, titanium combines directly at elevated temperatures with many nonmetals such as hydrogen, oxygen, nitrogen, the halogens, boron, carbon, silicon, and sulfur. Titanium compounds such as the nitride (TiN), carbide (TiC), and the titanium borides TiB and TiB_2 are interstitial, quite stable, quite hard, and refractory. Because these compounds form a surface film on the elementary metal, they are able to protect it from corrosion, with a subsequent improvement in its mechanical properties.

In the presence of hydrogen, titanium becomes brittle; its mechanical properties are all but destroyed. Because the atomic radius of hydrogen is so small, it can invade the lattice structure of titanium, filling the empty spaces. The result is an expansion of the lattice with a cor-

ANATASE—Like rutile, anatase is a form of titanium dioxide. The sample in this illustration is anatase on magnetite, of the type mined in Switzerland.

responding weakening of the forces holding it together; hence, the brittleness.

When cold, titanium is impervious to the action of most mineral acids; it dissolves readily only in hydrofluoric acid. Whether cold or hot, it is totally unaffected by aqueous alkali solutions. Traditionally used as a component in special steels, titanium is now primarily used in the aerospace and defense industries. The metal is produced in large quantities in the United States and the Soviet Union.

Titanium is used in alloy with many metals, among them aluminum, chromium, manganese, vanadium, molybdenum, and zirconium. Its properties are substantially improved when alloyed. Titanium alloys are used, for example, to build aircraft parts and engines having the structural and chemical stability of steel without the weight of steel. In some instances, titanium or an alloy is the only usable metal. A case in point is the type of tank used for storing liquid oxygen in rockets. The liquefied gas, at temperatures around −190° C (−310° F), causes ordinary metals to become brittle and useless; a titanium-aluminum-vanadium alloy withstands such temperatures superbly.

ILMENITE—Elementary titanium is extracted from ilmenite, rutile, and sphene. A ferrotitanate, $FeTiO_3$, ilmenite forms trigonal crystals.

THE CHEMISTRY OF TITANIUM

Titanium is found in three oxidation states, +2, +3, and +4, with the last forming the most stable compounds. Bivalent titanium compounds are rare and do not exist in moist environments because they are oxidized by water.

Of most interest to the chemist is trivalent titanium. Compounds of this oxidation state are obtained by the electrolysis or chemical reduction of aqueous solutions of the tetravalent salts. In water, the complex $Ti(H_2O)_6{}^{3+}$ ion imparts a violet color to the solution. The most important trivalent salts are the halides.

Perhaps the tetravalent titanium compound of greatest importance is titanium dioxide, TiO_2. Possessing considerable opacity, it is used as a brilliant white paint pigment. From the technical viewpoint, the halides, especially titanium tetrachloride, $TiCl_4$, are important; the tetrachloride is used to obtain the pure metal. In water or moist air, titanium tetrachloride hydrolyzes to produce hydrochloric acid and titanium dioxide. During this reaction, great quantities of dense white smoke are produced. More than just a laboratory curiosity, this reaction is used to produce smoke screens and has been used in skywriting.

In combination with metallic cations, tetravalent titanium forms a series of compounds called titanates. These can be subdivided into two isomorphous series: the ilmenites, $FeTiO_3$, which include titanates of magnesium, manganese, cobalt, and nickel; and the perovskites, $CaTiO_3$, which include strontium and barium titanates.

While there is no such compound as titanic acid, a hydrated form of titanium dioxide, with the possible formula $Ti(OH)_4$, is known. A qualitative test for the presence of titanium involves the treatment of a tetravalent salt solution with a peroxide (hydrogen peroxide, for example). The resultant yellow precipitate is due to the formation of a complex titanium peroxide. This reaction can reveal even minute quantities of titanium.

Inorganic chemists do not lay sole claim to the use of titanium compounds. Recently, it was discovered that complexes of titanium tetrachloride with alkyl derivatives of aluminum are extremely efficient catalysts in the polymerization of olefins.

PEROVSKITE—The illustration shows an excellent sample of perovskite crystals on a rock base. These large monoclinic crystals, $CaTiO_3$, are fairly typical of this relatively widespread mineral.

TITANITE—Also known as sphene, titanite is a complex mineral with the formula $CaTiOSiO_4$. It forms monoclinic crystals that range from greenish to yellow to colorless. The crystals are hard and lustrous. The sample shown is titanite on chlorite.

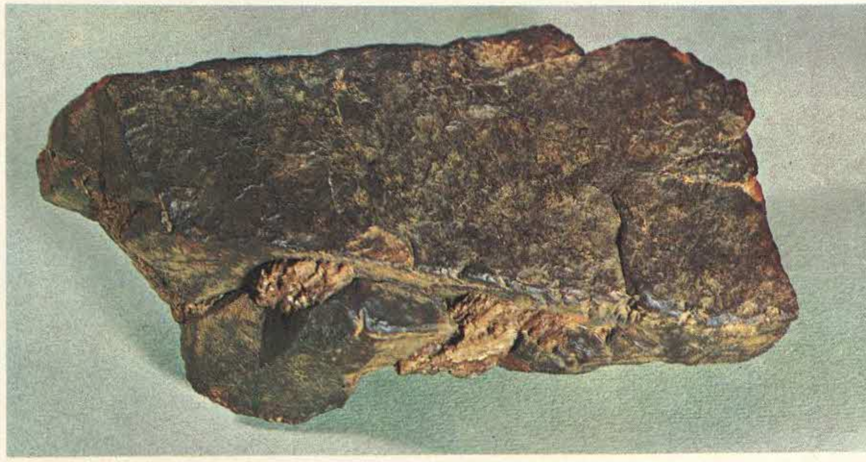
NIOBIUM AND TANTALUM | an almost inseparable union

Niobium (Nb) and tantalum (Ta), discovered in 1801 and 1802, respectively, are rare metals with only slight geographical distribution. Since the two are always found together in nature, and since both exhibit similar properties, the difficulties surrounding their original discovery and final isolation are understandable.

In 1801, working with an ore sent to England by the first governor of Connecticut more than a century earlier, the English chemist Charles Hatchett discovered an element unknown until then. In honor of America, the source of his ore, he named this mysterious metal columbium. The following year, the Swedish chemist A. Ekeberg discovered tantalum under similar circumstances. This element draws its name from a character in Greek mythology, Tantalos the father of Niobe.

For many years, many chemists considered columbium and tantalum to be the same element. In 1844 the German chemist Heinrich Rose, and later, in 1866, the Swiss chemist J. C. G. de Marignac, demonstrated that niobic and tantalic acids were two distinct compounds. In his research, Rose actually dealt with only one element, which he called niobium. Originally, his belief led him to conclude the existence of two metals, a mistake growing out of his work with compounds in which niobium showed different oxidation states. What was more, Rose's metal had properties identical to those of columbium, forcing him to conclude that he had rediscovered the element discovered 40 years previously by Hatchett. Thus, chemistry was in the somewhat unique situation of having one element with two accepted names: columbium and niobium. It was not until 1950 that niobium became the officially recognized name for the metal.

The most extensive deposits of niobium and tantalum have been found in Africa, Canada, Norway, and the United States. Niobium is found in columbite-tantalite (containing iron, manganese, tantalum, and oxygen in addition to niobium), euxenite (composed of niobates, tantalates, and titanates of rare earths), and



COLUMBITE OR NIOBITE — This somewhat rare ore is a ferrous metaniobate in isomorphous mixture with tantalite. It always contains some manganese, and may include tin and tungsten. It crystallizes orthorhombically. This sample is from Madagascar.

pyrochlore (a complex of niobium, calcium, fluorine, oxygen, and sodium). Tantalum ores include fergusonite (a rare earth tantalate), tantalite, microlite (containing tantalum, calcium, and oxygen), and samarskite. The latter contains twelve elements in addition to tantalum and is mined in the Urals of the Soviet Union.

REFINING METHODS

Because niobium and tantalum have strikingly similar properties and are al-

EUXENITE—An isomorphous mixture of rare earth niobates and tantalates with titanates, this ore forms orthorhombic crystals. The sample shown here was found in Norway; the ore varies in color from black to brown to greenish.

PYROCHLORE—A calcium niobate with sodium fluoride, pyrochlore sometimes contains the corresponding tantalate in isomorphous mixture. It forms cubic hexoctahedral crystals that can be colorless, yellow, or brown, as in this sample from Canada.

ways found together in nature, the problems in refining are obvious. In addition to being separated from the other elements in their ores, niobium and tantalum must be isolated by somewhat complex processes.

Generally, the ores are fused with sodium carbonate to produce sodium niobates and tantalates. When treated with hydrochloric acid, insoluble hydrated oxides are precipitated. These, in turn, are mixed with hydrofluoric acid to produce salts of the elements, each with different degrees of solubility. Thus, they can be separated by fractional crystallization.

The oxide of niobium produces the oxyfluoniobate anion $NbOF_5^{2-}$, whose salts are very soluble, and the tantalum oxide forms the heptafluotantalate anion TaF_7^{2-}, forming less soluble salts. Thus, the metals are obtainable from their separated compounds; tantalum by direct sodiothermy from the fluotantalate and niobium by aluminothermy from its pentoxide.

Tantalum is remarkable in its inertness. This property has made it a valuable tool in surgery, where it is used to replace bone, especially in the skull. The metal is also used in neurosurgery to tie severed nerves, and as a fine webbing to fasten muscle tissue in abdominal operations.

Niobium lends special properties to steel alloys, imparting greater strength to both ferrous and nonferrous metals. In special alloys it is also a superconductor, and a special niobium-zirconium wire is able to retain its superconductivity even in the presence of strong magnetic fields. The latter property may find use in the direct, large-scale generation of electric power. Some niobium alloys are used in atomic energy reactors because of properties that include low resistance to thermal neutrons.

THE CHEMISTRY OF NIOBIUM

Niobium is a platinum-gray metal with a brilliant luster. It acquires a bluish cast when exposed to air at room temperatures for prolonged periods. With respect to physical properties, it differs from tantalum primarily in its greater fusibility and lesser ductility. It is completely unaffected by all acids except hydrofluoric, but is attacked by alkalis in the fused state. Hot hydrogen will also react with the metal. Niobium reacts slowly with carbon, and combines with nitrogen at relatively low temperatures to form a nitride. These two compounds are interstitial in structure, since the carbon or nitrogen occupies the free spaces between the niobium atoms.

NIOBIUM +3 AND +4 COMPOUNDS

It is possible to produce compounds of niobium in the trivalent state, though none have been definitely isolated. In theory, these should be obtainable by the electrolytic reduction of niobic acid, H_3NbO_4, in a sulfuric acid bath on a platinum cathode.

The existence of niobium dioxide is known, although the oxidation state of the metal is not precisely known. The metal's ions may be present in a 1:1 ratio of the +3 and +5 states. In any case, the dioxide is an inert black powder obtained by reducing niobium pentoxide.

NIOBIUM +5 COMPOUNDS

Like all of the Group VB elements, the pentavalent state of niobium is the most stable. Known pentavalent compounds include the pentoxide, Nb_2O_5, a white, fairly stable powder that is insoluble in acids or water. When fused with alkalis, it yields niobates that are stable in aqueous alkaline solutions.

There are several classes of niobates: the orthoniobates, having the general formula Me_3NbO_4 (where Me represents an alkali metal), the metaniobates $MeNbO_3$, and the hexaniobates $Me_8Nb_6O_{19}$.

Niobium also combines with the halogens in its +5 state, in many cases by direct reaction with the halogen. For example, niobium chloride is formed by heating the metal in the presence of elementary chlorine. Niobium pentafluoride was first obtained by treating the pentachloride with hydrofluoric acid. An oxychloride is another of the niobium halides. While they are solid materials, the halides of niobium are rather volatile; the oxyhalides are less so.

THE CHEMISTRY OF TANTALUM

The value of this metal in the pure state certainly outweighs the difficulties of refining. Tantalum is extremely ductile and is highly resistant to most common acids. The metal is silvery in color and luster, and similar to platinum in some respects. In addition to its use in surgery, it functions as a catalyst in the manufacture of

synthetic rubber. Special steels incorporate traces of tantalum, and it is sometimes used to replace platinum, which is also virtually insoluble in acids. Tantalum is also used in components of electron tubes and rectifiers.

Presently, tantalum is obtained by the reduction of potassium heptafluotantalate, K_2TaF_7. The metal produced in this way is quite pure, although certain applications demand that it be purified even further. Like niobium, tantalum absorbs hydrogen when hot, and reacts with carbon and nitrogen to form the carbide and nitride that are similar to those of niobium. Tantalum carbide, an extremely hard material, is used as an abrasive and in cutting tools used in machining steel.

The existence of bivalent, trivalent, and tetravalent compounds of the metal is known, but they are little more than laboratory curiosities at present. As yet, they have not been isolated with ease because of a marked tendency to oxidize rapidly.

COMPOUNDS OF +5 TANTALUM

Except in minor respects, the pentavalent tantalum compounds behave like their niobium homologs. Tantalum pentoxide is a white powder, soluble only in hydrofluoric acid. It is easily obtained by burning the metal in air. This compound, when fused with alkalis, forms tantalates, which are homologs of the niobates; these include the orthotantalates and the alkaline hexatantalates, $Na_8Ta_6O_{19} \cdot nH_2O$.

Tantalum halides include the pentafluoride, pentachloride, and bromide. The chloride is prepared by treating tantalum pentoxide with carbon tetrachloride in the presence of chlorine:

$$Ta_2O_5 + 5CCl_4 \xrightarrow{Cl_2} 2TaCl_5 + 5COCl_2.$$

The pentachloride is immediately hydrolyzed by water unless some hydrochloric acid is present. The reason is probably due to the formation of the somewhat unstable hexachlorotantalic acid, $H(TaCl_6)$. Tantalum pentafluoride and pentachloride are crystalline, colorless, and similar in appearance to their niobium equivalents.

FERGUSONITE—A tantalate of yttrium, iron, and rare earths, fergusonite also contains tin and tungsten. Certain varieties are rich in titanium. The crystals of fergusonite are tetragonally shaped, and its color ranges from gray to brown to yellow. The sample in this illustration was found in Norway.

MICROLITE—A tantalate of calcium in combination with sodium fluoride, microlite is often found in isomorphous mixture with the corresponding niobium ore pyrochlore. Like pyrochlore, its crystals are cubic hexoctahedral. This sample was found in North Carolina.

RADIUM AND ASTATINE | a basis for atomic physics

At about the same time that the German physicist Wilhelm Roentgen discovered x-rays, the French physicist Henri Becquerel began investigating the relationship between the fluorescence of certain minerals and their emission of penetrating rays. His experiments led to the discovery that some natural fluorescence is independent of exposure to x-rays. Part of his proof was based on the fact that photographic paper could be exposed by certain fluorescent minerals even though the paper was shielded from visible light. Fluorescent radiation, therefore, was much more penetrating than light radiation, and quite distinct from Roentgen's x-radiation. These new rays came to be known as Becquerel rays.

Becquerel's research was soon followed by the discovery that his rays had nothing at all to do with fluorescence. It was demonstrated that several nonfluorescent materials have identical Becquerel ray emission properties. The Polish physical chemist Marie Curie discovered that thorium was one such substance. The emission property was given a new name—radioactivity. Radioactivity is intrinsic in matter and independent of any chemical process; thus, it cannot be studied as a chemical reaction.

The next in this series of discoveries came when Marie and Pierre Curie began their now-famous work with uranium. They noticed that the ores and derivatives of uranium displayed the property of emitting Becquerel rays more distinctly than pure uranium. Since no radioactive element was known at that time, the Curies postulated that uranium ores contained a strongly radioactive new element.

Following this tack, the Curies treated pitchblende (a uranium oxide ore) with various reagents, separating small quantities of other elements from it. The two scientists found that one of the elements often associated with uranium—bismuth —was extremely radioactive when precipitated as bismuth sulfide. Furthermore, when the sulfide was dissolved in hydrochloric acid and a silver wire immersed in the solution, the radioactivity was transferred to the wire. This offered proof that an unknown element was present in pitchblende, and Madame Curie called this element polonium in honor of her native Poland.

Another element contained in uranium ores and showing radioactive properties was barium, which the Curies precipitated as barium sulfate. This led them to conclude that a second unknown element had been discovered. To recover it, they converted the sulfate to the bromide and subjected the latter to fractional distillation, obtaining not only barium bromide, but other bromides with varying degrees of radioactivity. In particular, one bromide compound appeared to exhibit marked radioactivity. In 1898 the Curies succeeded in isolating 0.1 g of the bromide of the unknown element from about two tons of pitchblende, and called their discovery radium (Ra). Radium's existence had been predicted by Mendeleev, who left a blank space for it in his periodic table.

Once this highly radioactive element had been discovered and isolated, the Curies launched an exhaustive study of the nature of the powerful radiation emitted by certain elements. With the aid of special electrical fields, they proved that the emissions of radium were of three different types. The first were particles with a +2 charge and a mass of 4; the Curies called these alpha particles. The second type consisted of particles with a charge of −1, but with a mass too small to be measured; these were named beta particles. A third type was a powerful emission similar to x-rays but of higher frequency, which the scientists called gamma rays. The painstaking research of the Curies led the English physicist Ernest Rutherford to theorize that these particles and rays were due to the elimination of matter and the corresponding liberation of enormous amounts of energy. All of this opened the way to Albert Einstein and his atomic physics.

Radium is the most important of the radioactive elements. In contrast to uranium and thorium, the most stable isotope of radium, with an atomic weight of 226, has a relatively short half-life of 1,620 years. The other isotopes, with which it is in equilibrium and which it produces as disintegration products, have considerably shorter half-lives. Radium is also the easiest of the natural radioactive elements to obtain in a pure state in measurable quantity, and it provides the basis for a scale of radioactive measurement. The curie has been adopted as the unit of measuring the radioactivity of a given source, whether natural or artificial. This unit is defined as the radioactivity of a given quantity of a substance decaying at the rate of 3.7×10^{10} disintegrations per second. In the case of radium this quantity is one gram.

THE CHEMISTRY OF RADIUM

Radium is an alkaline-earth metal of Group IIA in the periodic table. Like the other elements in this group, its physical and chemical properties are determined by its electron structure. The Group IIA

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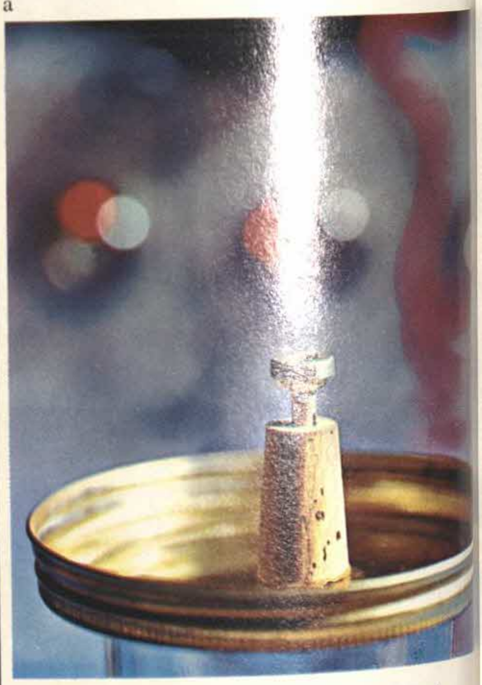


OBSERVING RADIUM—A preparation based on radium-226, like that in Illustration 1a, is often used to carry out simple observations of the properties of alpha, beta, and gamma radiation. The material contains radium and its decay products, with a radioactivity of about

elements are characterized by the two electrons in their outermost shells. This explains not only their +2 valence, but also why their ions are smaller than those of the neighboring alkali metals.

Chemically, radium is similar to barium, only somewhat more active; and like all the more electropositive metals, radium liberates hydrogen from water at ordinary temperatures. The salts of radium include the carbonate, $RaCO_3$, which is only slightly soluble in water. This salt is identical in structure to calcium carbonate. Radium sulfate, like barium sulfate, is almost totally insoluble in water. Radium chloride is a soluble salt produced indirectly from the sulfate.

RADIUM AND HUMAN PHYSIOLOGY

Radium and its salts appear harmless enough; however, the unseen alpha, beta, and gamma radiation present a serious radiological hazard to living tissue. Therefore, an upper limit of exposure has been established amounting to two roentgens per month, and a total body content concentration of 0.1 microgram.

On contact with the skin, radium causes reddening, swelling, and ulceration, as a result of the superficial penetration of alpha and beta particles. Such injury is not painful, but healing is difficult. Prolonged contact presents greater physical danger from powerful gamma radiation, which is deeply penetrating, causing damage to deeper tissues such as lymphatic cells, reproductive cells, and embryonic cells.

The gamma radiation of radium can be a two-edged sword, however. Since it destroys rapidly growing cells (embryonic cells, for example), it can be used in the treatment of certain types of cancer. However, the introduction of artificial nuclides has largely replaced the use of radium in cancer treatment.

Introduced into the human organism, radium causes an increase in cellular oxygen consumption, thus causing acceleration of the metabolic processes. In large or prolonged doses, however, it causes serious anemia and eventual death. A witness to this is the number of deaths of persons working with radioactive materials without observing necessary safety precautions.

ASTATINE

Element number 85, astatine (At), is a member of Group VIIA in the periodic table, sharing its place with the halogens. These elements are characterized by the seven electrons in their outermost shells, and by a strong tendency to complete these shells by acquiring an eighth electron. Like the halogens, astatine has a common valence of −1, although it can assume positive valences as well.

Astatine was discovered in 1940 at the University of California by Emilio Segrè, K. R. Mackenzie, and Dale R. Corson, following the bombardment of bismuth with alpha particles:

$$^{209}Bi_{83} + \alpha^{4}_{2} \rightarrow {}^{211}At_{85} + 2n^{1}_{0}$$

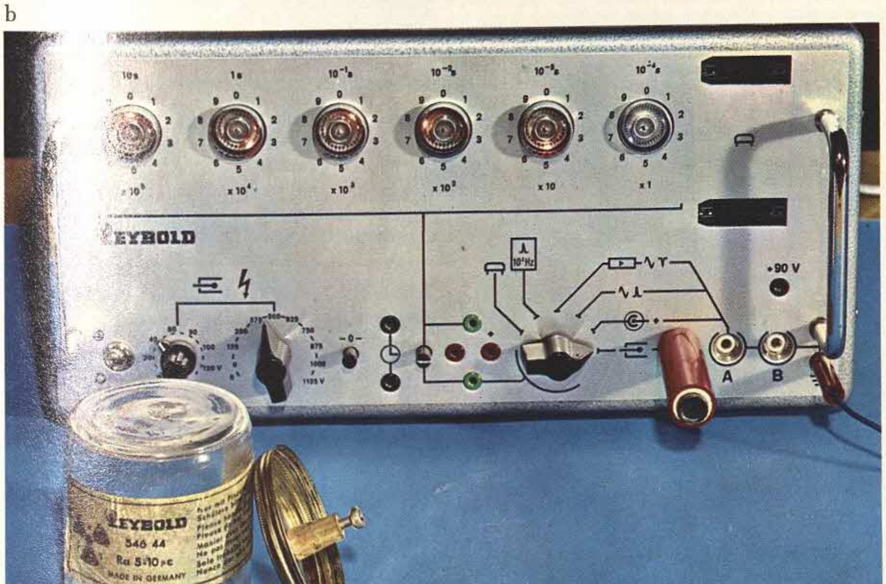
The name astatine is derived from the Greek *astatos* meaning "unstable."

The isotope thus produced has a half-life of 7.5 hrs and shows a dual decay; about 60 percent of the atoms emit alpha particles of 5.94 Mev (million electron volts) energy and transform into ^{207}Bi, and the remaining 40 percent transform by orbital electron capture to ^{211}Po (AcC′), which in turn emits alpha particles of 7.43 Mev energy to become ^{207}Pb (AcPb). About 20 isotopes have been identified.

Astatine also occurs naturally as a disintegration product of uranium-238, uranium-235, and thorium-232. Its most stable isotope, astatine-210, has a half-life of only 8.3 hrs, while astatine-216 has a half-life of less than 0.001 sec—explaining why so little is known of its chemistry.

Astatine is believed to be analogous in many respects to iodine, although somewhat more metallic. Like iodine, it collects in the thyroid gland. In the presence of an alkali hydroxide, elementary astatine behaves according to the dismutation reaction typical of the halogens, producing an ion with a +1 charge, and one with a −1 charge. An affinity for silver is also known. When a solution containing Ag^+ ions is reduced in the presence of astatine, the latter precipitates completely onto the silver.

b



9 microcuries (corresponding to about 9 micrograms of pure radium). The radioactive substance is contained in the metal capsule affixed to the cork, and is stored in a glass container. The glass itself does not allow passage of the slow alpha and beta particles, so the material must be removed from the container to study these radiations. Powerful gamma rays are not stopped by the glass, however. Illustration 1b is a counter—an electronic device that measures the number of particles emitted per second.

GERMANIUM | raw material for transistors

The element germanium (Ge) was discovered in 1886 by the German chemist C. Winkler, in argyrodite, a double sulfide of the element and silver. Winkler named the new element in honor of his native land.

ARGYRODITE—This sample, mined in Bolivia, is the type of mineral in which germanium was first discovered. It is a germanium-silver sulfide that forms orthorhombic crystals. The mineral is found as small crystals, or as a compact black mass with blue and purple highlights.

1

Germanium's existence had been predicted by Mendeleev, who assigned a blank space for element number 32 in his periodic table. This unknown material was dubbed ekasilicon and some of its properties were correctly predicted before its discovery.

Germanium ores, which are not widely distributed, include argyrodite from Germany and Bolivia and the thiogermanate now mined in South Africa. Traces of the element are also found in association with zinc in its ores and in many silicates. However, the presence of germanium in most coal deposits assures a substantial future supply.

Pure germanium is a crystalline, brittle, lustrous, grayish-white metal. Its cubic structure is similar to that of diamond, and the metal is classed among the electrical semiconductors.

3

PROCESSING METALLIC GERMANIUM—One of the by-products of zinc refining is crude germanium dioxide, the starting point for obtaining the pure metal. The crude dioxide is converted to the tetrachloride, $GeCl_4$, which is hydrolyzed into pure germanium dioxide. The

2

GERMANITE—Not a crystalline mineral, germanite is invariably seen in reddish-gray compact masses having a metallic luster. Chemically, it is a sulfide of copper, iron, and germanium, although it may contain zinc, gallium, and a rather high percentage of arsenic. This sample was mined in South Africa.

THE CHEMISTRY OF GERMANIUM

Germanium is quite stable at normal temperatures, but when heated it oxidizes to germanium dioxide, GeO_2. It is from this oxide that the metal is obtained by reduction with either hydrogen or carbon.

The metal is decomposed by such strong oxidizing acids as nitric, while reducing acids such as hydrochloric do not attack it. Dilute alkali hydroxides dissolve germanium to form germanates.

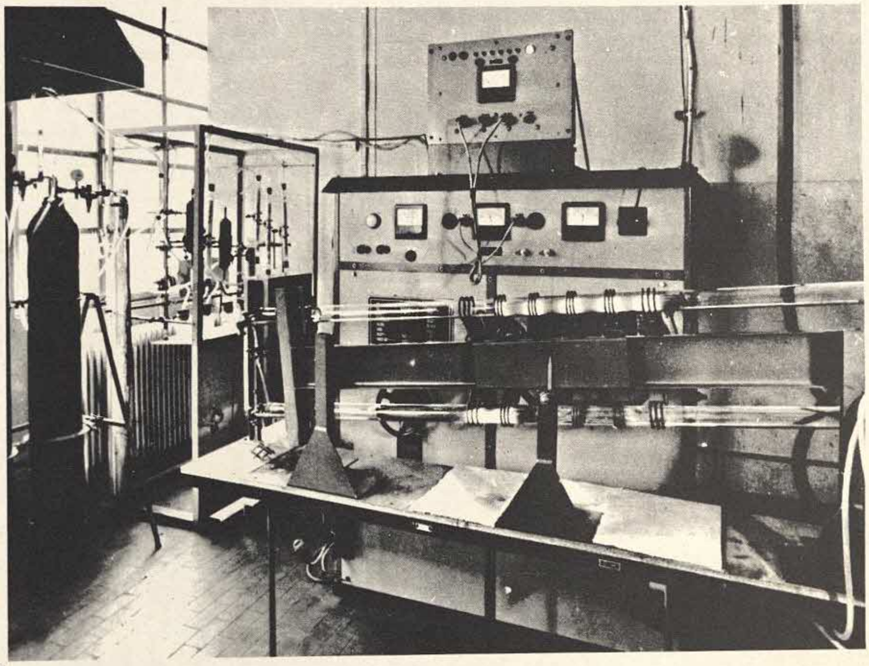
Germanium reacts with all of the halogens; the tetrachloride is, in fact, one of the starting points for procurement of the pure metal. Germanium tetrachloride reacts vigorously with water to form the dioxide, and from the latter the metal is obtained by reduction:

$$GeCl_4 + 2H_2O \rightarrow GeO_2 + 4HCl$$
$$GeO_2 + 2H_2 \rightarrow Ge + 2H_2O.$$

illustration shows resistance furnaces in which this pure dioxide is reduced at about 1,150° C (2,102° F). The resulting metal is 98 percent pure, and further refining can produce a purity of 99.9 percent.

4

a



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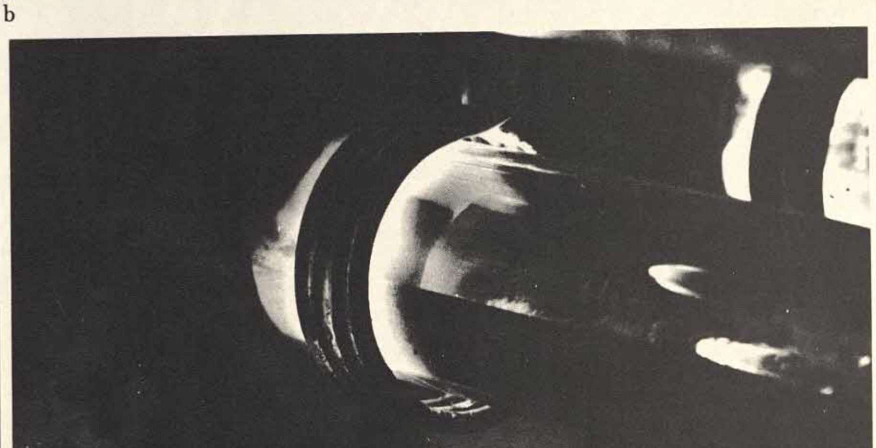


ZONE FUSION OF GERMANIUM—The refining of germanium into pure ingots takes place in a microwave furnace (Illustration 4a). Illustration 4b shows a quartz tube containing a graphite cylinder that encloses the ingot. A copper coil surrounds the entire tube.

Germanium dioxide is a white, crystalline compound that is isomorphous with silicon dioxide above 1,033° C (about 1,891° F). Below this temperature, it is an isomorph of cassiterite, a dioxide, SnO_2, of tin. In reality, there are two dioxides of germanium, one insoluble in water, the other slightly soluble. In solution, the soluble form produces colloidal germanic acid, H_4GeO_4, a weak acid.

While compounds of germanium and silicon are similar, their chemical properties allow these elements to be separated with relative ease. For example, germanium sulfide can be precipitated from strongly acidic solutions with hydrogen sulfide, while silicon compounds do not react in this way.

Germanium forms bivalent and tetravalent compounds; the latter have the greater stability. The bivalent materials are all strong reducing agents, and include germanium oxide, GeO. A black powder is obtained from the dioxide. Bivalent germanium halides, such as the dichloride, can result from the reaction between the tetrachloride and elementary germanium: $GeCl_4 + Ge \rightarrow 2GeCl_2$.

The reactions of bivalent germanium compounds are analogous to those of tin and lead, in that only two electrons are involved. The two electrons remaining

5

GERMANIUM INGOT AFTER ZONE FUSION—Following reduction of the dioxide, the germanium ingot is subjected to the zone fusing process. It emerges in three "zones," the first accounting for about 75 percent of the ingot's length and consisting of the pure metal, ready for use. The second zone, about 15 to 20 percent of the length, still contains impurities, and is reprocessed. The final 5 to 10 percent of the ingot's length is so full of impurities that it must undergo the same treatment as if it were a germanium ore. The illustration shows the surface of an ingot after zone fusing. (450 X)

in the valence shell combine to form an electron pair.

GERMANIUM AND ITS USE

Because of its properties as a semiconductor, germanium has an important role in the electronics industry. When the metal is doped with gallium or arsenic impurities, it is used in transistors, the miracles of miniaturization that have replaced so many vacuum tubes. The inclusion of impurities allows the germanium electrons to react to thermal agitation, pushing them into a frenzy of activity that allows efficient flow of electricity. The impurity, whether arsenic or gallium, actually replaces some of the germanium, leaving free energy levels into which electrons of the metal can move.

Besides its use in transistors, germanium is used as a component of photoelectric cells, as a phosphor in fluorescent lamps, and as an alloying agent in metallurgy. In addition, because of its high index of refraction and dispersion, germanium is used in making glass for high-quality photographic and microscope lenses and objectives. Of increasing importance is the field of organogermanium chemistry, wherein certain germanium compounds demonstrate a marked activity adverse to many bacteria while maintaining a low level of physiological toxicity. Such compounds show prospects of being effective chemotherapeutic agents.

RUTHENIUM AND OSMIUM | the only elements with a valence of eight

Ruthenium and osmium are members of Group VIII in the periodic table, sharing that group with rhodium, palladium, iridium, and platinum. The last element gives the group its name—the platinum series. It is quite common to find all of these elements together in nature, and separation can be difficult due to similarities in their properties.

Ruthenium and osmium are hard, brittle metals with extremely high melting points. Like the other Group VIII elements, they are very resistant to the effects of acids. The processing of these metals is closely allied with platinum production. In one method, an ore containing all six elements is treated with aqua regia to dissolve all the metals but iridium, osmium, and ruthenium. The last two are converted to their tetroxides and finally reduced to the pure metals.

METALLIC RUTHENIUM—Ruthenium is a hard, brittle metal. This sample, gray and similar in appearance to iron, is the rarest of the platinum metals.

RUTHENIUM ACETYLACETONATE—The most stable compounds of ruthenium are those in which the metal is trivalent. This compound has the formula $Ru(CH_3COCHCOCH_3)_3$.

THE HISTORY OF RUTHENIUM AND OSMIUM

The discovery of ruthenium is generally credited to the chemist C. Claus. In 1844, he was able to recover about 6 g (about [illegible] oz) of the metal from a residue of crude platinum dissolved in aqua regia. This element is named for the country from which this ore came (Ruthenia is Latin for Russia).

Osmium was discovered by the English chemist S. Tennant in 1803, in a residue similar to that in which Claus found ruthenium. Osmium takes its name from the Greek *osme*, a smell. The reference is appropriate, since one form of the metal releases odorous osmiun tetroxide in air.

Both metals are found in the native state, and are most often associated with platinum. They are also found as the sulfides in certain nickel-bearing ores. Such ores are found in commercial quantities in the Urals and in North and South America. The Sudbury, Ontario, region is a rich source of nickel-bearing ore.

THE CHEMISTRY OF RUTHENIUM

The rarest element in the platinum series, ruthenium is a white, hard metal, having four crystal modifications. Insoluble in all acids, including aqua regia, it does react with the halogens and with hydroxides. While ruthenium exhibits valences from 0 to 8, the number of its compounds is small. One such compound, ammonium ruthenium chloride, is processed commercially in order to obtain the pure metal.

Present applications for ruthenium include its use as a catalyst in oxidation reactions, and it is one of the most effective hardeners known for platinum and palladium. In alloy with these metals, the products are extremely resistant to wear, and electrical contacts are the primary products. The corrosion resistance of titanium is markedly increased by the addition of ruthenium.

The oxidation state of +2 is stable in only a limited number of compounds. Ruthenium trihalide, dissolved in an excess of a halogen acid, forms a complex, dark blue ion, RuX_4^{2-} ($X =$ the halogen). Compounds of this ion, treated with alkalis, produce a precipitate of $Ru(OH)_2$. This compound readily oxidizes in air to the somewhat more stable $Ru(OH)_3$. Another bivalent ruthenium compound is the cyanide, $Ru(CN)_2$. In an excess of cyanide ions, this produces the $Ru(CN)_6^{4-}$ ion, whose salts are among the most stable of +2 ruthenium compounds.

Ruthenium ions in the +3 state produce even more stable compounds. For example, the metal reacts directly with chlorine to form ruthenium trichloride, and the hydroxide of bivalent ruthenium changes spontaneously into $Ru(OH)_3$. This, in turn, is rapidly converted into the more stable ruthenium dioxide, which is RuO_2.

Tetravalent ruthenium compounds include the chlorohydroxy acids, from which ruthenium tetrachloride can be produced, according to the reaction

$$Ru(OH)_4 + 4HCl$$

$$\rightarrow H_2[Ru(OH)_2Cl_4] + H_2O$$

$$H_2[Ru(OH)_2Cl_4] \xrightarrow{HCl} RuCl_4 + H_2O.$$

In the presence of moisture, $RuCl_4$ loses some chlorine to form $Ru(OH)Cl_3$.

The tetrachloride is the only ruthenium tetrahalogenide yet isolated. While the halogenoruthenates are relatively stable, they are easily reduced or hydrolyzed to $Ru(OH)_4$.

The only pentavalent compound of ruthenium is the fluoride, RuF_5. This compound is easily prepared by direct synthesis from the elements at around 300° C (about 572° F). Ruthenium pentafluoride is an unstable solid, decomposing even in the absence of air to its component elements. This solid melts at 101° C (213.8° F).

Compounds of +6 ruthenium include the ruthenates, with the general formula Me_2RuO_4, in which Me represents a univalent metal. Compounds of this type are similar in stability to the ferrates (compounds of the same general formula, with iron replacing ruthenium). The ruthenates are produced by fusion with alkalis, in the presence of oxidizers, from either elementary ruthenium or its lower valence compounds. The crystalline compounds that result are hygroscopic, prismatic, and blackish-green in color—although they become orange in solution. The ruthenates are readily reducible according to the reaction

AN ORGANIC RUTHENIUM DERIVATIVE—This compound demonstrates the rather complex chemistry resulting from the many valence states of ruthenium. The formula for this salt is $RuCl_3(NO)\ [Sb(C_6H_5)_3]_2$; its name, the rather imposing rutheniotrichloronitrosobis-triphenylantimonate.

A BIVALENT RUTHENIUM-ORGANO SALT—All of the salts of ruthenium are vividly colored; this complex organic derivative is no exception. Its formula is $RuCl_2\ [Sb(C_6H_5)_3]_4$. It, too, uses almost every letter in the alphabet in its name: rutheniodichlorotetrabis-triphenylantimonate.

METALLIC OSMIUM—Very similar to ruthenium in appearance and properties, osmium is found in crude platinum in percentages ranging from 1 to 10 percent. It is the most costly of the platinum metals and has the highest melting point—3,050° C (about 5,520° F)—of any platinum metal.

$$Me_2RuO_4 + 3H_2O \rightarrow 2Me(OH) + Ru(OH)_4 + 1/2O_2.$$

Perruthenates are compounds of ruthenium in a +7 oxidation state, having the general formula $MeRuO_4$. They are similar to permanganates, and are obtained by ruthenate dismutation:

$$3K_2RuO_4 + 2H_2O \rightarrow 2KRuO_4 + RuO_2 + 4KOH.$$

Perruthenate crystals are octahedral and dark in color, having a metallic luster, and are soluble in water in which they become dark green. Although these compounds are similar to the permanganates, they are less stable, and are primarily of an autocatalytic nature.

The only octavalent compound of ruthenium is the tetroxide. This and the tetroxide and sulfide of osmium are the only chemical compounds containing elements in the +8 oxidation state. Ruthenium tetroxide is obtained from the treatment of potassium ruthenate in an excess of chlorine:

$$K_2RuO_4 + Cl_2 \rightarrow 2KCl + RuO_4.$$

The tetroxide is a water-soluble orange solid, and is quite volatile. It and ruthenium tetrachloride are sources of the pure element. The concentrated fumes of ruthenium tetroxide are quite poisonous and explosive. Because of an ozone-like odor, the compound is easily detected, even in trace amounts. This material is used in organic chemistry for its excellent oxidizing properties. It readily distills from aqueous solutions.

THE CHEMISTRY OF OSMIUM

Similar to ruthenium, osmium is an extremely hard, brittle metal with a bluish-white luster. It is highly resistant to acid attack, though it oxidizes easily to its tetroxide when heated.

Osmium is the densest of all known metals, with a density of 22.48 g/cm^3. Only iridium (density 22.42 g/cm^3) approaches osmium in this area.

Because of its affinity for hydrogen, osmium in the finely divided state is used as a reducing agent.

Osmium forms compounds with its valences of 2, 3, 4, 6, and 8, the lowest valence state seen in complexes with carbon monoxide [$Os(CO)_5$ and $Os_2(CO)_9$, for example], although such complexes are very unstable.

Bivalent osmium dichloride is an insoluble, nonvolatile compound obtained by the reduction of osmium trichloride. It is a dark brown, deliquescent solid, not unlike its ruthenium homolog. The dichloride is a dismutation product of the trichloride at temperatures around 500° C (932° F):

$$2OsCl_3 \rightarrow OsCl_2 + OsCl_4.$$

It is water-soluble, and dissolves in alkalis to produce $[OsCl_3(OH)_3]H_3$ and $Me_3[OsCl_6]$, respectively.

Osmium dioxide, OsO_2, is a compound in which the element is found in its +4 oxidation state. This compound exists either as brown or black crystals or powder, and is a product of the reduction of osmium tetroxide. The tetrachloride and tetrafluoride are other +4 osmium substances.

Compounds of hexavalent osmium include the osmiates, characterized by the OsO_4^{2-} ion. Like the ruthenates, they are produced by the fusion of metallic osmium, or an osmium compound, with alkalis in the presence of oxidizers. They are less stable than the ruthenates because they tend to absorb oxygen and form compounds of octavalent osmium.

The only known octavalent osmium compounds are the tetroxide, OsO_4 and the sulfide OsS_4. The oxide is a colorless-to-light-yellow solid with a melting point around 40° C (104° F). The stability of this compound, however, remains up to 130° C (266° F). It is slightly soluble in water, and in alkali solutions it forms $Me_2[OsO_4(OH)_2]$.

While some researchers claim the existence of osmium tetrasulfide, others dispute this. Presently, therefore, its chemistry is open to speculation based on similar compounds.

Osmium tetroxide is an extremely toxic compound; in very low concentration it causes respiratory complications and skin or eye damage. Exposure can cause temporary blindness. Nonetheless, it finds some use in criminology to detect fingerprints and in microscope slide preparation. The metal is an efficient hardener for other metals, and is used almost completely in the production of hard alloys.

PROCESSING RUTHENIUM AND OSMIUM—These metals are obtained as a valuable by-product of platinum refining. The equipment shown in the illustration extracts the metals from crude platinum and separates them as complex ammonium salts. The ruthenium and osmium are subsequently converted to tetroxides or tetrachlorides and finally to the metals.

SELENIUM, TELLURIUM, AND POLONIUM | sulfur's higher homologs

Selenium (Se), tellurium (Te), and polonium (Po) share membership in Group VIA of the periodic table with oxygen and sulfur. These elements exist in several allotropic forms, differing in molecular complexity or crystalline structure. As the atomic number increases, the elements in this group tend to form long rows of atoms with covalent bonds. The resulting chains account for such properties as the elasticity of sulfur and the somewhat more stable structure of metallic selenium.

SELENIUM COMPOUNDS—Selenium was discovered by the Swedish chemist, J. J. Berzelius in 1817, and this illustration is of a collection of selenium compounds on which he conducted basic research. These samples are presently housed in the Swedish Academy of Science.

The structural complexity of the Group VIA elements increases from the diatomic oxygen molecule to metallic polonium because of increasing atomic size. Thus, the formation of multiple bonds increases proportionately to the bonding radius of the atom.

The valences of these elements range from −2 to +6, with those of −2, +4, and +6 representing the oxidation states for selenium and tellurium, and +2 and +4 for polonium.

SELENIUM

In 1817, the Swedish chemist J. J. Berzelius discovered that the process of roasting an ore containing copper, iron, and sulfur to obtain sulfur dioxide left a red, powdery deposit. Analysis of this dust showed it to be composed of tellurium and some unknown element. Whatever this unknown was, it was difficult to separate from the tellurium (named from the Latin, *tellus*, for "earth"). Berzelius thus called his discovery selenium, from the Greek *selene* for "moon," in honor of this close relationship.

Selenium occurs only rarely, and only in small quantities in the Earth's crust. Its presence has been observed in the solar spectrum. It almost always is found as the selenide in nature, and as such can often be found in small quantities with sulfides.

The eruption of Vesuvius in 1895 produced fumaroles containing large amounts of the element. Traces in agricultural soil render the soil unfit for use, though such selenium contamination is infrequent.

Selenides include berzelianite, Cu_2Se, tiemannite, HgSe, and naumannite, Ag_2Se—all rather rare minerals.

The primary source for metallic selenium is the residual mud from the refining of copper ores. A less important process allows the recovery of the metal from sludge remaining after the roasting of pyrites.

In air, selenium burns with a light blue flame, producing the dioxide, which has an unpleasant garliclike odor. Selenium dioxide is also produced when the metal is dissolved in concentrated sulfuric acid. Occurring in several allotropes, selenium may be amorphous (black in the vitreous state, and red as a powder or colloid), or crystalline (monoclinic crystals are red while hexagonal crystals are gray). At normal temperatures, the gray, hexagonal structure is the most stable. Here, the atoms are bound together in spiral chains, one atop another throughout the crystal's length. In the other crystalline forms, the molecular units are composed of eight atoms in a ring structure similar to that of sulfur.

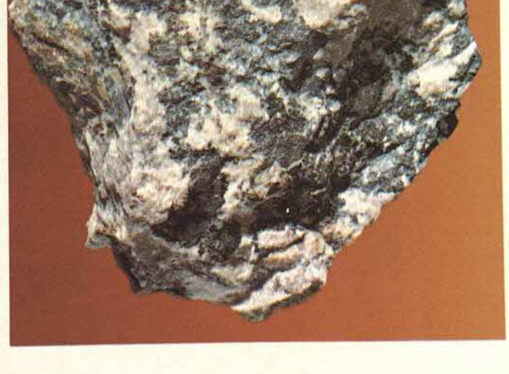
While amorphous selenium is a poor electrical conductor, in its crystalline form the element exhibits the property of electrical photoconductivity. This property stems from the fact that light striking crystalline selenium increases its conductivity. Hence, selenium finds use in photoelectric cells—so-called electric eyes. The basic element in such a cell is a copper plate on which a thin layer of selenium is deposited. This layer is covered with a thin, translucent film of gold leaf. The copper and gold are connected in a circuit, and if no light falls on the cell, no current is passed. However, when the cell is exposed to light, the selenium allows electricity to pass, and the circuit is closed. In addition, the amount of light striking the cell determines the degree of conductivity.

Selenium is also used in rectifiers that convert alternating current to direct current. A rectifier is similar in construction to a photoelectric cell, except that a lesser metal than gold is used—usually an alloy. The conversion is accomplished at the point of contact between the selenium and the alloy, which acts as a one-way gate for electrons.

In addition to its use in electronics, selenium is employed in glassmaking. Small quantities of the metal can neutralize the greenish tinge imparted to glass by iron impurities, while in larger amounts selenium gives glass a dark ruby color. For this reason, selenium is an ingredient in the red glass used in traffic lights.

Among the compounds formed by sele-

BERZELIANITE—This copper selenide has a metallic luster and silvery color, and crystallizes isometrically. Its primary sources are Germany, Sweden, and Argentina.



nium is hydrogen selenide, H_2Se, obtainable by direct synthesis at about 400° C (752° F), or by the action of hydrochloric acid on ferric selenide, FeSe. Hydrogen selenide is a colorless, vile-smelling gas that is extremely toxic. Actually, all selenium compounds are considered hazardously toxic and must be stored and handled with utmost care. Strangely enough, elemental selenium is almost completely nontoxic. The gas is used to precipitate many heavy metals as their respective selenides.

Selenium dioxide, SeO_2, also colorless, is prepared by burning the metal in an excess of oxygen. This compound dissolves in water to form the weak selenious acid, H_2SeO_3.

Selenic acid, H_2SeO_4, is produced when selenic anhydride is dissolved in water, or when selenious acid is oxidized with potassium permanganate or chlorine. The analog of sulfuric acid, selenic acid is a somewhat weaker acid, but is a more powerful oxidizing agent. Selenates are isomorphous with sulfates and similar to them in chemical behavior.

TELLURIUM

In 1782, while studying Transylvanian gold minerals, the German chemist F. J. von Reichenstein found a theretofore undiscovered element in association with the antimony and bismuth in one of the minerals. He called this new material "metallum problematicum." The German chemist M. H. Klaproth undertook the study of this new element, and while trying to determine its properties was led astray by some of its characteristics. Its luster, for example, coupled with other qualities, deceived him into believing that this unknown matter was a noble metal. However, in 1798 he discovered his mistake and was able to identify tellurium, a name chosen from the Latin *tellus,* for earth.

Tellurium is sometimes found in the native state, or in combination with sulfur or a sulfur-selenium complex. Primarily, however, the metal occurs as tellurides. Its chief minerals are tetradymite, Bi_2Te_3, hessite, Ag_2Te, altaite, PbTe, and sylvanite, $(Ag, Au)Te_2$. The element can be isolated from tellurium-bearing sulfides, using several steps. The sulfides dissolve in hydrochloric acid, forming a solution containing tellurous acid, H_2TeO_3. This acid is further treated with sulfur dioxide, which causes metallic tellurium to be precipitated as a black amorphous powder.

When heated in air, tellurium burns with a blue flame tinged with green. In the process, it gives off highly toxic yellow vapors of the dioxide. Human exposure to this compound, to the extent of only .01 mg/m^3 of air, produces an intense, foul-smelling "garlic breath" that may be evident for months. This phenomenon is probably caused by the formation of methyl telluride within the body.

Hydrogen telluride (H_2Te) is a colorless gas that is not stable at room temperature. Like other tellurium compounds, it is also highly toxic, and like elemental tellurium, it burns in air to form the dioxide.

Dissolved in nitric acid, tellurium reacts to form tellurous acid, H_2TeO_3, which, when oxidized with chromic acid, forms orthotelluric acid, H_6TeO_6. This compound differs from its sulfuric and selenic analogs in that the six oxygen atoms are arranged in an octahedron around the single tellurium atom. This structure is not possible in the analogs for physical reasons; tellurium's atomic bonding radius is considerably larger than that of either sulfur or selenium. Though telluric acid is very weak, it does exhibit strong oxidizing properties.

ALTAITE—This lead telluride varies in color from gray to pale or bronze yellow. The major sources of this ore are the Altai Mountains in Mongolia and regions in Australia, Chile, and the United States. The sample in the illustration was mined in New Mexico.

POLONIUM

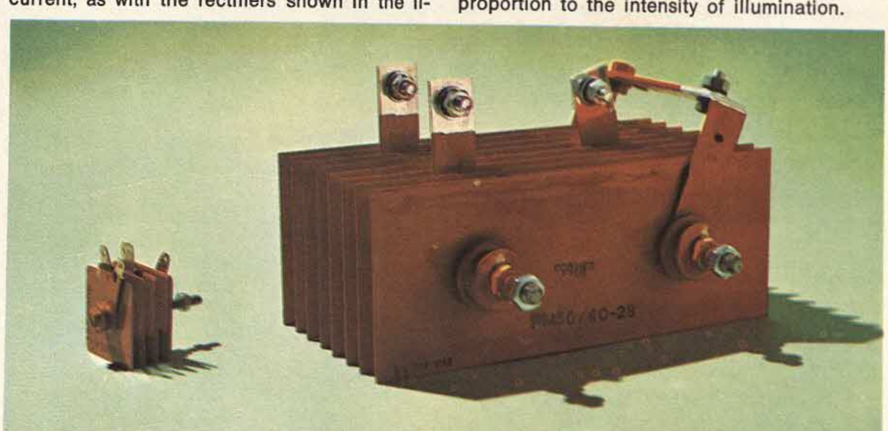
The final member of the sulfur family, polonium, was discovered by Pierre and Marie Curie in 1898. The element was named in honor of Mme. Curie's native Poland.

The nucleus of polonium is unstable, decaying to form a lead isotope by the emission of alpha particles. Strongly radioactive, a thousand times more so than radium, polonium presents handling problems. Additionally, extraction of the pure element is difficult; about 16 tons of uranium ore yield 3 mg of polonium salt. Nuclear bombardment of bismuth provides a more efficient source of the metal, but sophisticated equipment is required.

The most stable isotope of polonium has a half-life of 103 years, and its crystal lattice has been shown to be similar to that of tellurium. At low temperatures, polonium is cubic in structure, becoming rhombohedral as the temperature increases.

Compounds of polonium have limited application due to the metal's intense radioactivity and potent toxicity.

SELENIUM RECTIFIERS—Selenium acts as a semiconductor of electricity, and can thus be used to convert alternating current to direct current, as with the rectifiers shown in the illustration. Another important property of the metal is its photoconductivity. Light striking selenium permits the flow of electrons in direct proportion to the intensity of illumination.



MANGANESE | of glass and steel and semiprecious stone

Manganese (Mn), technetium, and rhenium, compose Group VIIB in the periodic table. Manganese is the most important of these elements because of its wide range of technical applications and its considerable natural occurrence.

Pyrolusite, an oxide of manganese with magnetic properties, was known to the ancient Greeks and Romans. In fact, its magnetic properties caused considerable disagreement among ancient philosophers. The element derives its name from the Latin *magnes,* owing to pyrolusite's magnetic characteristics, and from a corruption of Magnesia, a city of western Turkey (also called Manisa), where substantial quantities of the mineral have been found.

Manganese was recognized as a distinct element by several researchers before the pure metal was isolated by the Swedish mineralogist J. G. Gahn in 1774. The latter produced manganese by reducing pyrolusite with carbon. In 1882 the British metallurgist Robert Hadfield first processed manganese steel.

PROCESSING METHODS AND USES

About as much manganese as carbon is present in the Earth's crust; manganese exceeds sulfur in this respect. The metal, however, is not found in widely spread, rich deposits. Recently, however, exploration of the oceans has uncovered potentially large sources of manganese. The most common of the manganese ores are silicates, oxides, and carbonates. Major deposits are located in Brazil, Africa, India, and the Soviet Union.

The metal is obtained by reducing its oxides with aluminum, magnesium, or sodium, and by electrolysis. Because manganese ores often contain iron impurities, any metal not fully refined is really an alloy. However, most manganese is used in the iron and steel industries, so no great handicap is presented. In fact, certain alloys of iron and manganese are industrially important. Among these are ferromanganese (80 percent manganese and 20 percent iron) and spiegeleisen (20 to 30 percent Mn, 5 percent C, and the remainder iron). Such alloys are prepared by reducing mixed ores of the two metals with coal and carbon monoxide in a blast furnace. Refined manganese can be obtained by the electrolysis of aqueous manganous sulfate solutions in the presence of ammonium sulfate.

In the pure state, metallic manganese occurs in several allotropic forms. Since it is highly electropositive, the metal by itself is limited in use. In powdered form, manganese is very reactive, decomposing water and exhibiting pyrophoric tendencies.

Perhaps the greatest use made of manganese occurs in the steelmaking industry. To remove oxygen and sulfur impurities, small quantities of the metal are added during processing. The compounds formed with these elements are easily removed from the finished molten batch. Special steels, containing up to 14 percent manganese, are extremely hard, corrosion-resistant, and able to withstand considerable pounding and abrasion. Others contain manganese added during the hardening process, and these steels find use in ball bearings where distortion must be kept at an absolute minimum.

Manganese is also used in the making of nonferrous alloys; an example is manganese bronze. Alloys with aluminum, copper, and antimony are ferromagnetic,

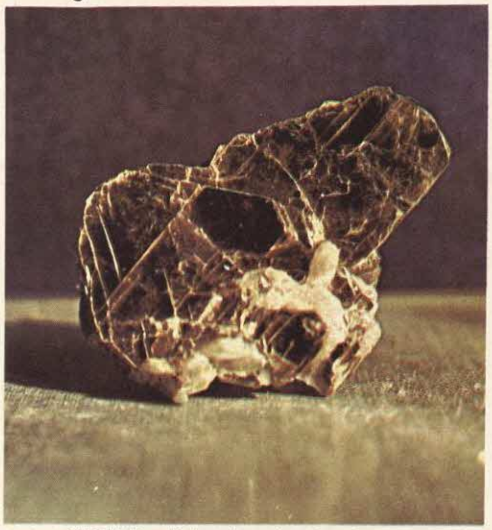
1

PYROLUSITE—This is manganese dioxide, the most common and most important of the manganese ores. Usually found in fibrous masses or in a granular, powdery form, it is dark, steel-gray in color, and generally opaque. On rare occasions it is found as pyramidal tetragonal crystals together with quartz, as in the illustration. Manganese dioxide produces beautiful dendrites in the crevices of rocks and in chalcedony. The largest deposits of this mineral are located in the Soviet Union.

2

TRYPHILITE—Generally found in gray-blue or gray-green masses, this mineral is a phosphate of lithium, iron, and manganese. Its luster is most frequently vitreous. Rarely it is located in isolated crystals of the orthorhombic type. The sample in this illustration was mined in New Hampshire.

3



BIOTITE — Belonging to the ferromagnesian mica group of minerals, biotite is a complex silicate containing eight elements in addition to manganese. Its crystals are monoclinic and are easily flaked into sheets, as are the crystals of micas in general. Biotite ranges from black to bright yellow in color, and appears to change color depending on the viewing angle (that is, it is pleochroic). It is found in many minerals in combination with quartz, muscovite, orthoclase, and amphiboles, and it occurs frequently in pegmatites.

despite the fact that none of the components have this property. Manganin, an alloy of 83 percent copper, 12 percent manganese, and 5 percent nickel, is used to make precision electrical resistors because of its low temperature coefficient.

The need for manganese as a trace element in animals and plants for healthy growth has been established.

THE CHEMISTRY OF MANGANESE

Manganese has valences of 1, 2, 3, 4, 6, and 7, although its stable compounds are formed only in the +2, +4, +6, and +7 oxidation states. At the higher valences, manganese produces stable anions, while at the lower end of the scale and as the elementary metal it behaves similarly to all metals.

Manganese is a typical transition metal, as can be seen from the number of its valences, its ability to form complexes, and the fact that some of its compounds are magnetic. Almost all manganese compounds are colored.

In the bivalent state, the manganous ion (Mn^{2+}) forms a great many stable salts. It is one of the few ions that is pale pink in color—due to a hydrated ion [$Mn(H_2O)_4{}^{2+}$]. Manganous sulfate, often crystallizing with four molecules of water, is a vitreous pink salt, and the sulfide forms green or pink crystals. Manganese carbonate is an interesting compound that decomposes readily, liberating carbon dioxide when heated. Manganous hydroxide occurs as the rare mineral pyrochroite.

Trivalent manganese salts are unstable in aqueous solution, decomposing spontaneously into bivalent and tetravalent manganese ions by dismutation:

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{++} + MnO_2 + 4H^+.$$

Trivalent manganese can be stabilized in several ways. For example, it can be combined with CN^- to form the complex [$Mn(CN)_6{}^{3-}$] ion; or it can be precipitated as the insoluble phosphate, $MnPO_4$, or hydroxide, $Mn(OH)_3$. Trivalent manganese oxide, Mn_3O_4, corresponding to the mineral braunite, is also stable because of its insolubility.

Compounds of tetravalent manganese include the important dioxide MnO_2. Manganese dioxide, known for centuries as a decolorizing agent in glassmaking, is a widely used oxidizer. In the glass industry, its actions are both chemical and physical: as an oxidizing agent, it produces carbon dioxide and colorless sulfates from carbon and sulfur impurities, respectively. Furthermore, a certain number of the tetravalent ions are converted to trivalent manganese. Since these are violet in color, they optically neutralize the green color imparted to glass by ferrous salts present as impurities.

A mixture of manganese dioxide and alkali carbonates, fused in air, produces a dark green mass. This is due to the formation of the manganate ion $MnO_4{}^{3-}$. This ion is stable in basic solutions, although in acids it will dismute to the dioxide and permanganate ion:

$$3MnO_4{}^{2-} + 4H^+ \rightarrow MnO_2 + 2MnO_4{}^- + 2H_2O.$$

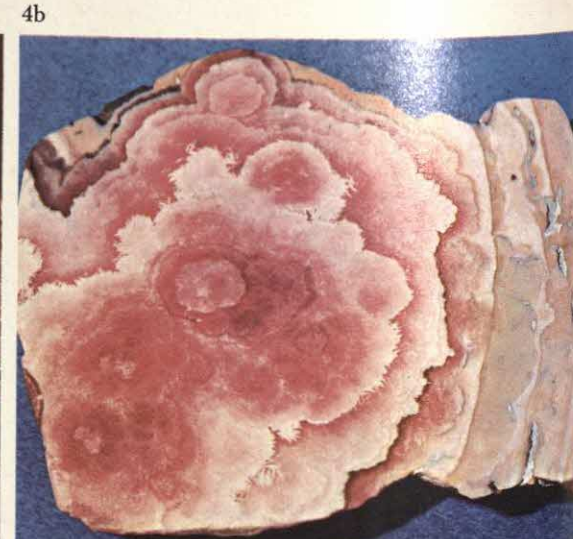
In the reaction, the solution changes from green to violet, signifying the presence of the permanganate ion.

The most important salt of +7 manganese is potassium permanganate. This salt is a powerful oxidizer, especially in

RHODONITE AND RHODOCHROSITE — Both minerals are semiprecious gems. The rhodonite in Illustration 4a is a manganese silicate whose color ranges from pink to red. The black areas are manganese dioxide. The best examples of rhodochrosite, a manganese carbonate, come from Argentina, as does the sample in Illustration 4b. Often, traces of iron, calcium, magnesium, and zinc replace some of this mineral's manganese. Rhodochrosite is almost always found in various shades of pink, with the colors arranged in bands. The mineral has a pearly, vitreous luster. It is less hard than rhodonite and has perfect rhombohedral cleavage.

4a

4b



5

a

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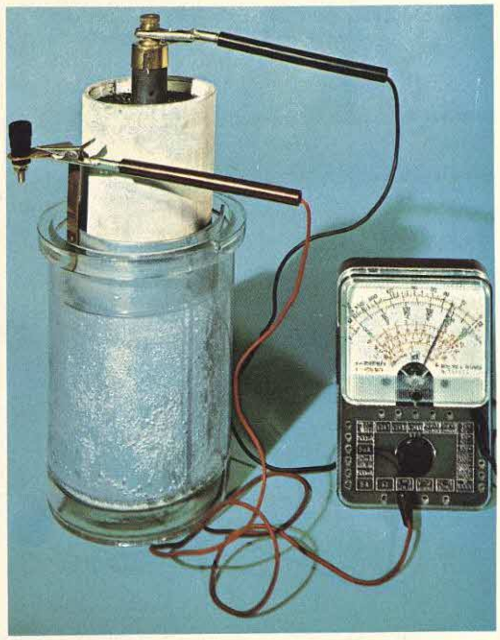


LECLANCHÉ CELL — Manganese dioxide is used in dry cells where the electrolyte is contained either by absorption or gelatinization. The illustration is of a Leclanché cell connected to a voltmeter. The negative electrode is a zinc cylinder, while the positive electrode is graphite. The electrolyte is a gelatinous solution of ammonium chloride. Hydrogen, liberated at the graphite electrode, is eliminated by a mixture of lampblack and manganese dioxide that acts as a depolarizer.

FERROMANGANESE—Manganese is alloyed with many metals, but finds its primary use in steelmaking. Manganese itself is not usually processed, since its iron alloy can be obtained from many ores. Illustration 5a shows the processing of ferromanganese by fusion of ores in electric furnaces. The ferromanganese in Illustration 5b contains 80 to 90 percent manganese.

the presence of acids. Here, it is reduced to bivalent manganese according to the reaction

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O.$$

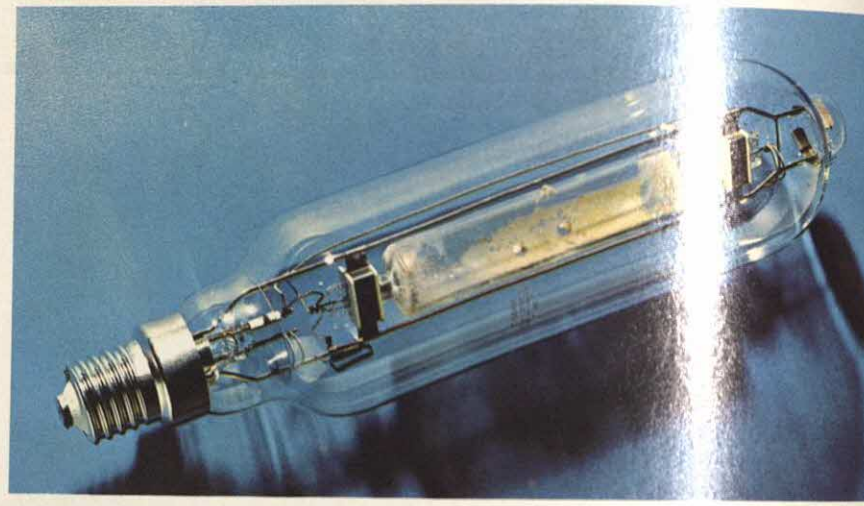
This reaction also undergoes a color change, thus making it useful in analytic chemistry as a titrating agent. Because it will oxidize many organic materials to the point of destruction, permanganate solutions are used as disinfectants, especially in the treatment of fungus diseases. Treating the permanganate ion with concentrated sulfuric acid produces the explosive oil manganese heptoxide. On the other hand, treatment with a neutral or alkaline material causes reduction to the tetravalent state.

GALLIUM, INDIUM, AND THALLIUM | bright lines in the spectrum

1

SAKURAIITE — Discovered only recently in Japan, this is the only known ore containing large quantities of indium. It has the composition $(Cu,Zn)_3InS_4$.

2



MERCURY VAPOR LAMP — The bluish-white light emitted by mercury vapor lamps is often undesirable from a color-rendering standpoint. To overcome this, sodium, indium, and thallium iodides are added to the mercury. The lamp shown here, containing indium and thallium iodides along with mercury, is typical of the type used to illuminate sports arenas.

The histories of these elements touch at several points, beginning with Mendeleev's prediction of their existence in the periodic table. Proof of this hypothesis came in the nineteenth century through spectroscopic analysis, and gallium (Ga), indium (In), and thallium (Tl) were confirmed as members of the family of elements.

Thallium was the first of the trio to be discovered. In 1861, while working in a sulfuric acid factory in Germany, the English physicist Sir William Crookes extracted a substance from the mud deposited in lead acid chambers. At first Crookes believed the material to be tellurium (a metal discovered much earlier). However, careful study with the aid of a spectroscope revealed a characteristic of some unknown element. What Crookes saw was a bright green line, now recognized as thallium's spectral "fingerprint." He named the new element thallium, from the Greek *thallos* meaning "green stalk"—an apt description of his observation. Although this element was at first thought to be similar to sulfur and selenium, later research showed that some of thallium's properties mimicked those of the alkalis.

The spectroscope was also responsible for the identification of indium. In 1863, the German mineralogists F. Reich and H. Richter examined bits of the mineral sphalerite spectroscopically and noted some indigo blue lines, indicating the presence of an unknown material. From their observations they named their discovery indium. This team later isolated the metal and catalogued its properties.

Gallium was discovered by the French chemist Lecoq de Boisbaudran in 1875. Again, the spectroscope played a key role in proving Mendeleev's theories. Among the spectral lines characteristic of aluminum, the French chemist observed some atypical features. Basing his research on the earlier theories, Lecoq de Boisbaudran correctly surmised the existence of gallium, a name he later chose to honor his native France (from the Latin *Gallia*). His work led to the final isolation of this strange metal by electrolysis of the metal hydroxide dissolved in potassium hydroxide.

Neither gallium, indium, nor thallium occurs in a free state. Rather, all are found as ores or as impurities in aluminum, lead, zinc, selenium, and sulfur compounds. While these metals are widely distributed, they are quite rare. Gallium and indium are almost always associated with aluminum, lead, and zinc ores. Trace deposits are found in Germany, Spain, and the United States. Thallium, the most abundant of the three elements, has as its ores crookesite, lorandite, and hutchinsonite, a complex mineral with the composition $(Pb,Tl)S \cdot Ag_2S \cdot 5As_2S_3$.

The three metals are characterized by their softness and low melting points. Additionally, they bear strong resemblance to one another, and their alkalinity increases in direct proportion to their atomic weights. Thallium, in fact, is similar in some respects to the alkalis and produces a univalent oxide, Tl_2O, that dissolves in water to form a strongly basic hydroxide, TlOH.

GALLIUM

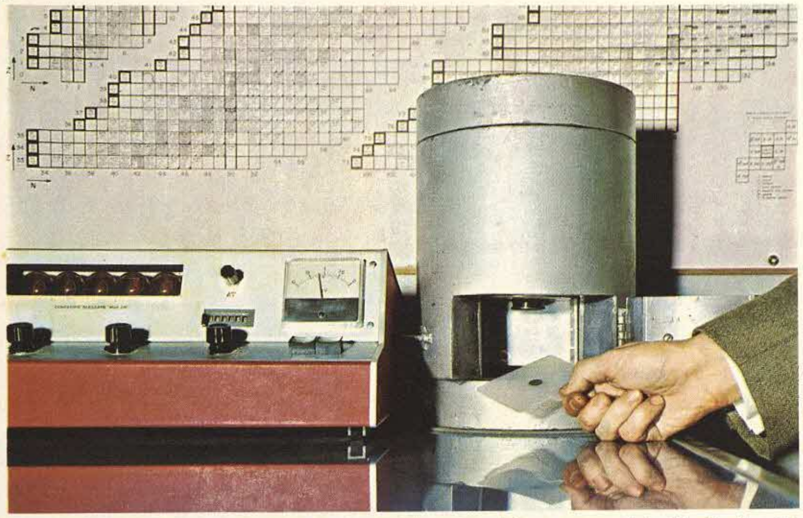
While this element is not the most scarce metal (its distribution is widespread), no gallium ores are rich enough to make direct extraction practical. Therefore, it is obtained as a by-product of the refining of other elements. To some extent, gallium always accompanies bauxite, and from this source it is produced secondarily by electrolysis of the aluminum ore.

In its purest form, gallium is a highly lustrous silvery metal, though it sometimes is seen with a bluish-white cast. It is one of the few metals that can be

3

a

b



KEEPING AN EYE ON RADIOACTIVITY—One present application for indium is in nuclear reactors. Disks of metallic indium (Illustration 3a) are used to record the flow of neutrons produced by atomic reactors. The disks are bombarded by the neutrons and the resultant artificial radioactivity measured. In Illustration 3b, a technician is placing an indium disk into a Geiger counter to measure its radioactivity.

liquid at normal temperatures, with a melting point just under 30° C (86° F). One of its unique features is a factor of expansion on the order of 3 percent on solidification. This metal is relatively unaffected by exposure to air, showing little affinity for oxygen.

Gallium is attacked slowly by hydrochloric acid, and to a lesser extent by nitric acid. Strangely, because it is less electropositive than aluminum, it should dissolve readily in nitric acid, and the reason for this behavior is not yet understood.

Alkaline solutions have a strongly corrosive effect on gallium, resulting in the formation of the hydroxogallate anion $Ga(OH)_4^-$. Characteristic of the Group IIIA elements, gallium's most common valence is +3, though it forms some bivalent compounds.

Gallium's trivalent oxide is easily obtained by roasting the metal in air, and from this compound the hydroxide $Ga(OH)_3$ can be formed. This hydroxide is isomorphous with its aluminum counterpart. Gallium hydroxide is a very weak base, and will solubilize to $Ga(OH)_4^-$ ions in an excess of alkali. Gallium sulfide and arsenide, two of the element's more important compounds, can be obtained by direct synthesis. The arsenide is a semiconductor, capable of converting electricity into coherent light, and finds use in lasers and other light displays.

The halogen compounds formed by gallium are similar to those of aluminum. Gallium fluoride, like aluminum fluoride, differs considerably from the other halides in its insolubility and high melting point. Gallium bromide and chloride are quite volatile and soluble in water. The importance of the fluoride lies in the formation of the $(GaF_6)^{3-}$ ion in an excess of reagent.

INDIUM

Indium is always found to some extent in the ores of zinc, lead, and aluminum. Therefore, it is an easy step to recover this metal as a by-product of the refining of these three primary materials. Indium is prepared by electrolysis or by reducing the oxide with carbon:

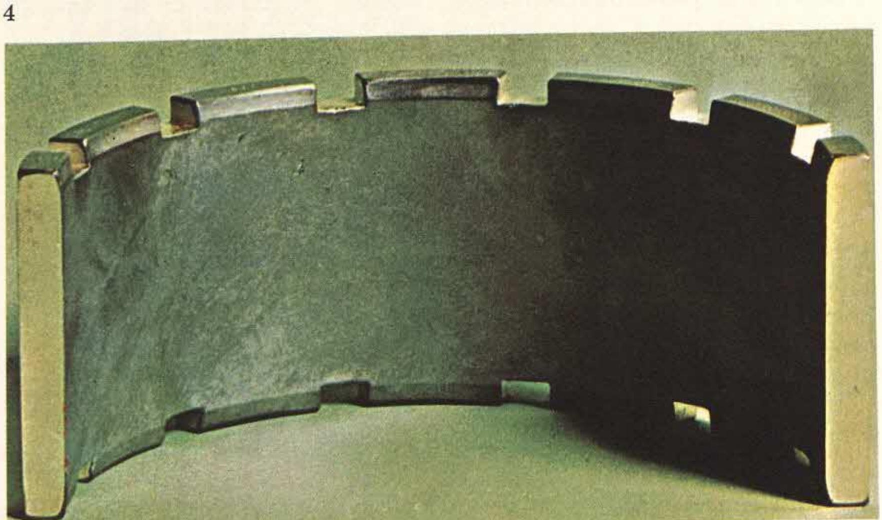
$$In_2O_3 + 3C \rightarrow 2In + 3CO.$$

In the pure state, indium is a soft, silvery-white metal that shows little effect on exposure to the atmosphere. It differs from gallium in that it is insoluble in alkaline solutions and evolves hydrogen in the presence of acids. The latter attests to the greater electropositivity of indium.

Indium forms compounds in a univalent and trivalent state, and possibly forms bivalent compounds. Its most stable configuration, like that of gallium, is +3. The trioxide and hydroxide are formed when the soluble salts of indium are precipitated with alkalis. Unlike gallium hydroxide, indium hydroxide does not solubilize in an excess of basic solution.

AIRCRAFT ENGINE BEARINGS—This section of a piston engine bearing incorporates several metals, among them a lead-indium alloy. Such an alloy withstands the tremendous corrosive action common to internal combustion engines.

4



5

HUTCHINSONITE—This mineral contains several elements, among them thallium. The prismatic crystals range in color from scarlet to dark cherry-red. Hutchinsonite is often found associated with other sulfides, and with sphalerite, pyrite, realgar, and orpiment.

6

SARTORITE—This mineral commonly has the formula $PbAs_2S_4$, with traces of thallium. The sample in this illustration contains about 4 percent of the element. The prismatic crystals, dark gray in color with a metallic appearance, may be several centimeters long.

Indium halides are prepared in ways identical to those used for the gallium analogs, and the sulfide is formed in the reaction between hydrogen sulfide and a soluble indium salt:

$$2InCl_3 + 3H_2S \rightarrow In_2S_3 + 6HCl.$$

The electronics industry is the primary user of indium, where it is used as a doping agent in semiconductor devices. In such a capacity, indium is found in a variety of products from transistors to photoelectric cells.

THALLIUM

Because this metal is often found in pyrite (FeS_2) and sphalerite (ZnS), thallium is a natural by-product of the sulfuric acid industry (in which iron pyrite is a raw material) and the zinc industry.

Thallium is a soft, bluish-white metal, oxidizing readily in moist air. It dissolves rapidly in nitric and sulfuric acids. It contrasts markedly with gallium and indium in the formation of univalent ions, and the compounds formed by +1 thallium are similar to the alkali metals and in certain respects, to silver compounds. Because trivalent thallium is a powerful oxidizer, compounds of this type are rapidly reduced to Tl^+ substances.

Thallium monoxide, Tl_2O, results when the metal is burned in air; the compound is a black, hygroscopic powder. The monoxide reacts with water, yielding a hydroxide with properties similar to those of the alkali metal hydroxides. Other univalent thallium compounds include the brown sulfide and a carbonate.

Thallium chloride is quite similar to silver chloride. Both are decomposed on exposure to light, whereby they are reduced to the elemental state.

Trivalent thallium compounds include a trioxide, Tl_2O_3, which is somewhat stable. However, at around 700° C (1,292° F) it loses oxygen and produces the monoxide and a weakly alkaline hydroxide. Trivalent thallic chloride is a product of the reaction between univalent thallous chloride and chlorine. Owing to the strong bond between the ions, thallic fluoride is a very stable compound.

Thallium must be stored and handled with care since it is a highly toxic material. Extremely small concentrations have an adverse effect on man and lower animals, hence its use in rodenticides. As a sulfide, the metal exhibits certain photoelectric properties and finds use in photo cells.

Thallium monoxide imparts high refractive properties to optical glass. It is used also to color artificial gems. Thallium acetate provides high-specific-gravity solutions for refining ores.

ZIRCONIUM AND HAFNIUM | two elements with the same properties

The element zirconium (Zr) is a grayish-white, lustrous metal that occurs with titanium and hafnium in Group IVB of the periodic table. While zirconium is considered one of the "new metals," its ores have been known for thousands of years.

The ancient Greeks probably used a zirconium ore as a gem; they called it hyacinth because of its burnt orange color. In his *Historiae naturalis* Pliny mentions other colored varieties of this stone, such as chrisolitos, melichrisos, and crateritis. Writing A.D. 300, the Greek philosopher and scientist Theophrastus was probably describing the mineral zircon, $ZrSiO_4$—the principal sources of zirconium—when he wrote about "lyncurium," an amber stone that became charged with electricity when rubbed and that was used to make seals. The name zircon comes from the Persian word *zargun*, meaning "gold-colored," the appearance of zirconium ore in its most common form.

In 1789 the German chemist M. H. Klaproth identified zirconium from its oxide in the mineral zircon. In 1824 the Swedish chemist J. J. Berzelius succeeded in isolating an impure state of zirconium. The next important advance did not come until 1925, when two Dutch scientists, A. E. van Arkel and J. H. de Boer, produced massive ductile metal from zirconium.

Zirconium accounts for 0.22 percent of the Earth's crust and is not, therefore, considered a rare metal. It is present also in some stars, in the sun, and in meteorites.

Besides zircon, the ores of zirconium include baddeleyite (brazilite), ZrO_2, found chiefly in Ceylon, Thailand, and Brazil; and zircite, a mixture of zirconium oxide and silicate, found in considerable quantities in Australia. Zirconium is extracted from both of these ores.

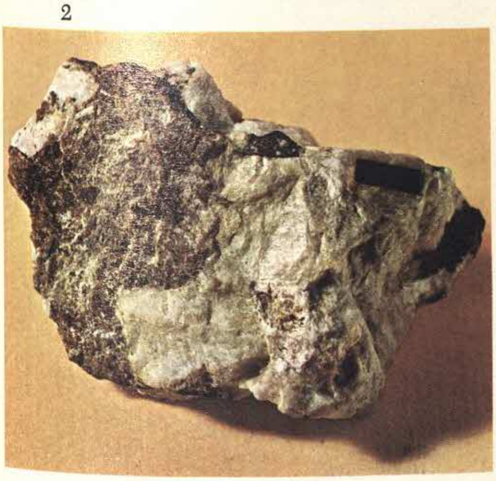
The element hafnium (Hf) occurs in zirconium ores in quantities varying from 1 to 5 percent, and is much less abundant than zirconium. It was discovered in 1923 by the Hungarian chemist G. C. de Hevesy and a colleague, D. Coster, who succeeded in isolating the element. The two scientists named it hafnium, the Latin name for Copenhagen, where the discovery was made.

THE CHEMISTRY OF ZIRCONIUM

Until a few years ago, zirconium was of little importance, and processing methods were unsophisticated. With the development of new technical equipment, extraction processes greatly improved. At the same time, zirconium was found to make a good jacket for uranium fuel rods in nuclear reactors—due to its excellent mechanical properties and its very low neutron-absorbing capacity. To serve this purpose, however, zirconium must be processed to a high degree of purity. Two different processes can accomplish this. The first—the Kroll process—involves fusing zircon or some other ore with carbon to produce zirconium carbide, which is then treated with chlorine to produce zirconium tetrachloride, $ZrCl_4$, which is purified by repeated sublimation. The zirconium tetrachloride is then reduced with magnesium to yield magnesium chloride and zirconium in the form of a spongy mass. The magnesium chloride and excess magnesium are removed by distillation and the metal is fused into

LAAVENITE—A zirconium ore that also contains a large percentage of extraneous ions, laavenite forms monoclinic crystals. Its formula is $Zr(Mg,Ca,Mn)_3$. It ranges in color from yellow to brown to black, and occurs as a product of magmatic separation in Norwegian syenites.

2



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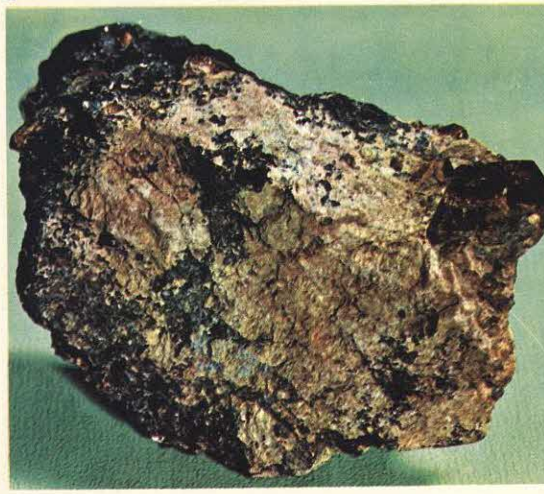
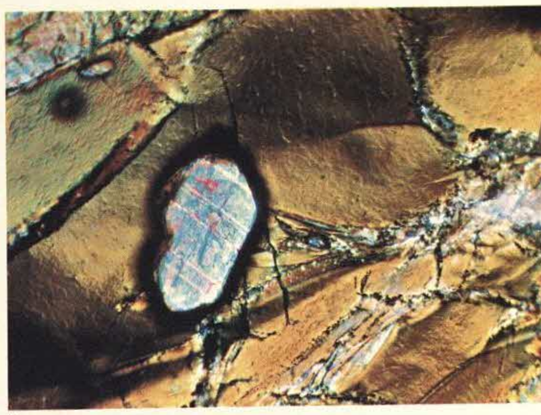




b

ZIRCON — Chemically a zirconium silicate, zircon is the chief ore from which zirconium is extracted. The ore is sometimes found as a monocrystal (Illustration 1a), but is more commonly a product of magnetic separation in granites. Illustration 1b shows a section of granite containing a zircon crystal seen through the microscope in polarized light. Zircon varies in color from green to brown, orange and blue; it may also be colorless. Zircon is mined in Ceylon, Thailand, Australia, and Canada; its clear varieties are used as gems.

3

ASTROPHYLLITE—A rare mineral, astrophyllite forms triclinic crystals. It occurs in more or less hexagonal crystals, often aggregated in the shape of a star—hence its name. Its color is bronze yellow and its luster is submetallic or mother-of-pearl. The sample in the illustration is associated with long riebeckite crystals and comes from the syenite pegmatites of Norway.

ingots in an inert atmosphere to avoid oxidation.

In the second method—the van Arkel process—the ores are reduced by treatment at high temperatures with calcium. After the calcium oxide has been removed, the impure metallic zirconium interacts with iodine at 200° C (392° F) to produce volatile ZrI_4. This is brought into contact with a filament of molybdenum or tungsten heated electrically to 1,300° C (2,372° F). At this temperature the compound decomposes into very pure zirconium—which deposits on the filament—and iodine, which returns to the cycle. The entire process is carried out in a vacuum to avoid reactions between the metal and atmospheric gases.

Neither of these processes separates zirconium from its constant companion, hafnium. Such separation is achieved either by fractional distillation of halides, by fractional precipitation of phosphates, or by treating phosphate solutions with ion-exchanging resins.

Zirconium is highly resistant to chemical reagents; only hydrofluoric acid and aqua regia corrode it. Zirconium reacts with oxygen to produce zirconium dioxide, ZrO_2, and with nitrogen and carbon to produce respectively the very hard zirconium nitride, ZrN, and zirconium carbide, ZrC. Zirconium is tetravalent except in its nitric compound and its boron compound, ZrB; like zirconium carbide, these compounds are interstitial, meaning that the atoms of the nonmetals occupy interstitial positions in the lattice of the metallic zirconium. Zirconium hydroxide, $Zr(OH)_4$, is amphoteric in character—it can react either as a comparatively strong base or as a weak acid, H_4ZrO_4—and it has a strong tendency to pass into the colloidal state.

Zirconium dioxide, ZrO_2, which is obtained by heating zirconium hydroxide, occurs in two allotropic forms, monoclinic and tetragonal. Soluble only in concentrated sulfuric acid, zirconium dioxide forms zirconates such as K_2ZrO_4 and K_4ZrO_3 when combined with fused alkalis. When treated with hydrogen peroxide, these zirconates produce fairly stable peroxyzirconates such as K_4ZrO_8. Zirconium dioxide has a high melting point of 2,700° C (4,892° F) and is used as a refractory.

Zirconium halides are produced by heating the metal with the halogen X

$$Zr + 2X_2 \rightarrow ZrX_4,$$

or by combining the dioxide with carbon in the presence of the halogen

$$ZrO_2 + 2X_2 + 2C \rightarrow ZrX_4 + 2CO.$$

The carbon reduces the dioxide to metallic zirconium, which then reacts with the halogen. Zirconium fluoride, chloride, bromide, and iodide are all solids that can easily be hydrolyzed in water to produce compounds of the type $ZrOX_2$.

Other salts include zirconium sulfate, $Zr(SO_4)_2$, which also occurs in hydrated form and as basic sulfates, and zirconium oxalate, $Zr(C_2O_4)_2$.

THE CHEMISTRY OF HAFNIUM

Zirconium and hafnium are in close proximity in their group in the periodic table and their atomic radii differ by only 0.01 Å (Angstrom): Zr = 1.595 Å and Hf = 1.585 Å. Their chemical behavior is therefore very similar, and chemical methods are ineffective in separating them. Only very refined and sophisticated techniques can extract hafnium from zirconium, and it is, therefore, seldom used except as a control element in nuclear reactors. Hafnium can be separated from zirconium in five different ways: fractional crystallization, selective extraction, ion exchange, fractional precipitation, and disproportionation or fractional distillation. Selective extraction, involving the preferential solubility of hafnium or zirconium in an organic liquid, is the preferred method.

MELANOCERITE—This complex mineral is a mixture of calcium, zirconium, and rare earth fluoroborates and fluorosilicates. It derives its name from its black, waxy appearance and occurs most commonly in the island of Kjeo in Sweden. The sample illustrated comes from the syenites mined in Ontario, Canada. Melanocerite has a hexagonal crystal structure.

4

SCANDIUM, YTTRIUM, AND THE LANTHANIDE SERIES | a long search for the rarest elements

Group IIIB is the largest "family" in the periodic table, and it includes those elements that are least abundant in the Earth's crust; hence, they are usually called the rare earths. The members of this group include scandium (Sc), yttrium (Y), lanthanum (La), and the 14 elements in the lanthanide series, and actinium (Ac) with its associated actinide series. In this latter series, at least 15 elements have been discovered.

The history of the discovery and isolation of these elements covers more than 150 years of research; the first member of the series was discovered in 1794 and the last in 1970. Though not the first member, yttrium (Y) was the first to be discovered as a result of analysis carried out by the Finnish chemist Johan Gadolin. He named his discovery after the Swedish town of Ytterby. In 1843, however, the Swedish chemist Carl Mosander found that yttrium was not one but three elements. Retaining the existing name for the most basic of the three, he called the others erbium (Er) and terbium (Tb).

Earlier in the century, the Swedish chemist J. J. Berzelius and the German chemist M. H. Klaproth had discovered cerium (Ce), an element whose name they derived from the asteroid Ceres, discovered in 1803. Following up on this work, and prior to his discovery of yttrium as more than one element, Mosander in 1839 was able to extract a minute quantity of lanthanum from cerium nitrate. The year was 1839, and from then on the discovery of more rare-earth elements came rapidly. Within the next 50 years, samarium (Sm) and dysprosium (Dy) were discovered, and scandium, gadolinium (Gd), and ytterbium had been identified. The Swedish chemist Per Teodor Cleve discovered both holmium (Ho) and thulium (Tm), while praseodymium (Pr) and neodymium (Nd) were identified and isolated. Around 1890, the existence of europium (Eu) was established.

In 1907, the French chemist Georges Urbain observed a dual personality in ytterbium, and further research led to his discovery of lutetium (Lu). At about the same time, element number 61 was thought to have been discovered independently in Italy and the United States. Hence, for 38 years it was called by two names: florentium and illinium. In 1945, with the birth of the atomic age, element 61 was definitely identified and permanently named promethium (Pm). Not found in nature, promethium is a result of neutron bombardment of other elements.

With the exception of promethium, all of the rare earths occur as ores, notably cerite, orthite, monazite, and gadolinite. The richest source of these ores is Scandinavia, while the United States and India provide sizable secondary deposits. The quantities of these elements in their respective ores vary considerably, with cerium the most abundant and lutetium the rarest (it is about 60 times less abundant than cerium).

THORTVEITITE—A scandium-yttrium silicate, $(Sc, Y)_2Si_2O_7$, that may also contain erbium, neodymium, and praseodymium, this mineral crystallizes monoclinically and is black or light gray in color. The sample in this illustration was found in Norway.

XENOTIME—This yttrium phosphate, YPO_4, may contain thorium, uranium, zirconium, beryllium, and calcium. Xenotime forms tetragonal crystals. If prismatic or pyramidal in form, it resembles zircon. This mineral also can be found as round grains with a vitreous or resinous luster ranging in color from yellow to red. While this sample comes from Madagascar, xenotime is commonly found in granites in Sweden, Norway, and Switzerland.

PROPERTIES

Scandium, yttrium, and lanthanum have three electrons each in their outermost shells (d^1s^2), as seen in the accompanying table. Chemically and physically, they are similar to calcium, strontium, barium, and radium—elements of Group IIA. This similarity to the alkaline-earth metals becomes more pronounced with cerium, where the electrons occupy the 4f rather than the 5d orbitals, although the outermost arrangement remains unchanged ($5s^2\ 5p^6\ 5d^{10}\ 6s^2$). This explains the chemical similarity of all the lanthanides. Nevertheless, because each succeeding lanthanide has one more electron than the element before it, there is a corresponding increase in the number of nuclear protons. Therefore, the ion radius decreases from one element to the next.

Corresponding to decreasing ion radii is a decrease in basicity of the metal hydroxides. The ion radius of cerium, for example, is 1.18Å, while samarium, four places later in the period, has an ion radius of 1.13Å. Thus, samarium is more metallic in character and its hydroxide is less alkaline than those of cerium.

Because of the difficulties encountered in the separation and isolation of the pure metals—due to their chemical and physical similarities—many properties of the lanthanides are still unknown. In the case of promethium, the amount of the material obtained is so small that most

MONAZITE—A phosphate of cerium and other rare-earth metals, particularly lanthanum, neodymium, and praseodymium, monazite also contains considerable quantities of mechanically held thorium silicate. The mineral forms monoclinic crystals, is radioactive, and has a resinous luster. Its coloring ranges from yellow to red, and it occurs as crystals in pegmatitic rock in the United States, the USSR, Norway, Sweden, but primarily in the monazitic sands of Brazil. The Brazilian deposits are exploited for their cerium and thorium content.

of its properties are still a mystery.

Some of the lanthanides have oxidation states directly related to the degree of saturation of their 4f orbitals. In theory, all lanthanides should exhibit greatest stability with a +3 valence, since all have three electrons in the outermost shell. In reality, a high degree of stability is shown by electronic configurations of $4f^0 \ldots 6s^0$, $4f^7 \ldots 6s^0$, and $4f^{14} \ldots 6s^0$; that is, there are zero, seven, and 14 electrons in the f orbitals and no electrons in the s orbitals.

For example, cerium has an outermost electron configuration of $4f^2\ 5s^2\ 5p^6\ 5d^0\ 6s^2$. This gives it a marked tendency to lose four electrons to stabilize at $4f^0\ 5s^2\ 5p^6\ 5d^0\ 6s^0$. However, the metal commonly exhibits a valence of +3 as well as +4. In a similar manner, ytterbium ($4f^{14}\ 6s^2$) easily gives up two electrons to acquire a $4f^{14}\ 6s^0$ configuration, demonstrating a very stable +2 valence state.

Characteristic of ions whose orbitals are not fully occupied is the range of color they impart to solutions. The lanthanides, whose 4f orbitals are partially filled, are no exception. The praseodymium ion is bright green, while neodymium forms violet ions, samarium and holmium yellow, and erbium pink. The lanthanum +3 ion, whose 4f and 5s orbitals are vacant, is colorless, as are scandium and yttrium ions.

PRINCIPAL USES OF RARE EARTHS

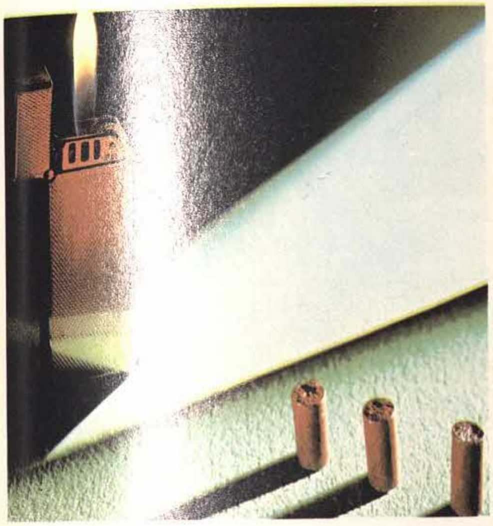
In the past, the main applications of rare-earth metals arose from group properties. As pure rare-earth metals and compounds became available, however, uses based upon individual properties were developed. These include the use of cerium (IV) oxide, CeO_2, as a highly effective glass polish, as a constituent to increase the stability and discoloration resistance of glass to gamma and electron-beam radiation, and as an opacifier for enamel coatings. Lanthanum oxide, La_2O_3, is used as a constituent of high-refraction and low-dispersion optical glass. There is some use of certain rare-earth oxides, chlorides, and phosphates as catalysts in organic reactions.

Certain compounds of lanthanum and yttrium showing unusual electronic or magnetic behavior are useful in microwave devices, magnetic core materials, and ceramic capacitors.

Nuclear applications, actual or potential, include the use of the elements of high absorption cross sections for thermal or slow-moving neutrons. Yttrium hydride, YH_3, is of use as a hydrogen-moderator carrier, and yttrium metal, as a construction material in reactors, because the metal is not attacked by the molten uranium at high temperature. Thulium and scandium, when suitably irradiated, serve as portable x-ray sources.

Certain rare earths have been useful stand-ins for the radioactive and fissionable elements. The use of cerium as a stand-in for plutonium and other trans-

ORTITE—A basic silicate of aluminum, iron, and calcium, this ore is rich in the rare-earth elements and belongs to the epidote group. It crystallizes in the monoclinic system, occurring as small greenish or black crystals in many granitic or porphyritic rocks. It is also found as large prismatic crystals in Sweden, Norway, and the USSR.



A PRACTICAL USE OF CERIUM—Cerium is the most widely used of the lanthanide metals—partly due to its relative abundance. Alloyed with iron, it is pyrophoric, thus finding use in flints for cigarette lighters.

uranium elements, for example, permitted scientists to devise methods for separating and identifying these newly discovered elements before weighable quantities had been prepared.

CHEMICAL AND PHYSICAL CHARACTERISTICS

The lanthanide metals are all silver-white in color, and are very reactive. In air, they readily produce compounds of the Me_2O_3 type in the +3 valence state (cerium produces CeO_2 due to the +4 state).

These elements also react with hydrogen to form MeH_2 or MeH_3, depending on the oxidation state. They are very electropositive, owing to their high oxidation potential.

Because of their relative scarcity, the lanthanides find limited use in industry. Nonetheless, they are important when incorporated into certain glassmaking processes, in metals and alloys, and in the production of radioactive materials.

EXTRACTION METHODS

Metallic scandium can be obtained by the electrolysis of fused potassium and scandium chlorides. In this process, the cathode is made of pure zinc, which can later be removed from the scandium by vacuum distillation. Like most metals, scandium is ductile and malleable. Yttrium is obtained by similar methods.

Lanthanum can be produced by reducing its chloride with potassium in an argon atmosphere. It is a ductile metal that corrodes in moist air to form the hydroxide, while in dry air its surface forms an oxide.

All the lanthanides can be extracted by reducing their halides with electropositive metals such as potassium. Separating them from one another depends on their varying degrees of alkalinity as hydroxides, and on the various oxidation states that some have.

LANTHANIDE COMPOUNDS

The compounds of scandium, yttrium, and lanthanum are all quite similar to one another. Included among the better-known compounds are the oxides Sc_2O_3, Y_2O_3, and La_2O_3. These are obtained by calcining the appropriate hydroxides in air. Each of these compounds is a white powder. The corresponding hydroxides are formed by the precipitation of their soluble salts in bases. In this form, they are gelatinous compounds whose solubility increases greatly from scandium hydroxide through lanthanum hydroxide.

These metals also form halides of the type MeX_3, and all of these compounds, with the exception of the fluoride, are soluble in water. Trivalent carbonates and sulfates can also be produced, each with varying degrees of solubility. For example, scandium sulfate is water-soluble while lanthanum sulfate is not.

Some of the most interesting lanthanide compounds are the nitrides, all of which are very hard and have high melting points. These properties are due to the position of the nitrogen atom in the crystal lattice. Filling the interstices between the lanthanide atoms, the nitrogen distorts the lattice's shape, which would otherwise be typically metallic.

Element	*Ion Radius*	*Outer Electron Configuration*	*Ion Color*
scandium (Sc)	0.83	$3d^1\ 4s^2$	colorless
yttrium (Y)	0.93	$4d^1\ 5s^2$	colorless
lanthanum (La)	1.15	$4f^0\ 5d^1\ 6s^2$	colorless
cerium (Ce)	1.18	$4f^2\ 5d^0\ 6s^2$	colorless
praseodymium (Pr)	1.16	$4f^3\ 5d^0\ 6s^2$	green
neodymium (Nd)	1.15	$4f^4\ 5d^0\ 6s^2$	violet
promethium (Pm)	?	$4f^5\ 5d^0\ 6s^2$	pink
samarium (Sm)	1.13	$4f^6\ 5d^0\ 6s^2$	yellow
europium (Eu)	1.13	$4f^7\ 5d^0\ 6s^2$	colorless
gadolinium (Gd)	1.11	$4f^7\ 5d^1\ 6s^2$	colorless
terbium (Tb)	1.09	$4f^9\ 5d^0\ 6s^2$	colorless
dysprosium (Dy)	1.07	$4f^{10}\ 5d^0\ 6s^2$	yellow
holmium (Ho)	1.05	$4f^{11}\ 5d^0\ 6s^2$	yellow
erbium (Er)	1.04	$4f^{12}\ 5d^0\ 6s^2$	pink
thulium (Tm)	1.04	$4f^{13}\ 5d^0\ 6s^2$	green
ytterbium (Yb)	1.00	$4f^{14}\ 5d^0\ 6s^2$	colorless
lutetium (Lu)	0.99	$4f^{14}\ 5d^1\ 6s^2$	colorless

BROMINE AND IODINE | the precious impurities in table salt

Atoms with seven electrons in the outer energy level tend to gain an electron from another atom. This completes or saturates the outer energy level with eight electrons, resulting in a particularly stable structure. These elements are, therefore, highly reactive. They combine readily with other elements—especially the alkali metals—whose atoms possess only a single electron in the outer energy level. Atoms of such metals lose the lone outer electron very readily. When the two atoms combine by the electron-exchange process described here, an ionic salt is formed. Those atoms with seven electrons in the outer energy level are, therefore, called halogens, from the Greek word meaning "salt generators."

There are five halogens: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). They are listed in the order of their increasing atomic weights; they increase in the same order with respect to chemical and physical properties. For example, at room temperature the first two are gases, the third is a liquid, and the last two are solids. The specific gravities and melting and boiling points also increase in the order given.

Of the five halogens, only the first four are found in nature. The fifth, astatine, does not occur in nature because all its isotopes are strongly radioactive. Moreover, it is not a product of the radioactive decay of other elements found in the Earth's crust. Even if astatine were present when the Earth was formed, it has long since disappeared completely as a result of radioactive decay. It is only because small quantities have been prepared in the laboratory that the element is known at all.

This article discusses the characteristics and properties of the elements bromine and iodine with brief mention of those of astatine. The properties and uses of fluorine and chlorine are so important they are described in a separate article.

THE ABUNDANCE OF BROMINE AND IODINE

Bromine and iodine are mostly found dissolved in water or in aquatic marine orga-

1

BROMINE—Both bromine and iodine are contained in seawater, but only bromine is extracted from seawater industrially. Shown here is a saltworks where the element is extracted from seawater that has been concentrated for the production of salt.

nisms. Both form highly soluble compounds. Thus, only negligible amounts are found in the rocks of the Earth's crust. These two elements are usually found together with chlorine compounds in the sea, since they have about the same degree of solubility. Bromine and iodine, however, are much rarer than chlorine. In the sea, bromine is about 200 times and iodine about 2,000 times rarer than chlorine. It is fairly easy to extract bromine from seawater that is concentrated for the production of salt. Iodine, on the other hand, is sought in richer sources because of its extreme rarity. Bromine and iodine are also found in salt deposits formed by the evaporation of seawater.

It is preferred, however, to extract iodine from richer sources than seawater or salts obtained by the evaporation of seawater. For example, the mother liquor obtained during the crystallization of sodium nitrate (Chile saltpeter) contains iodine as sodium iodate and sodium periodate. In the U.S., iodine is extracted from the brine found in California oil wells, where it is present as iodide. Another important source of iodine is seaweed. This piles up on beaches around the world, and is easy to collect. The seaweed is dried and burned. Iodine is then extracted fairly economically from the ashes, although a great deal is lost during the burning process.

DISCOVERY AND PREPARATION

Bromine was discovered by the French chemist Antoine Balard in 1826. Balard discovered it in the mother liquor of saline solutions and successfully extracted it in small quantities. Subsequently, methods were found for extracting bromine in much larger quantities, but only during the second half of the nineteenth century. Modern extraction processes are based on the collection of saline waters from brine wells in Michigan and West Virginia, where high bromide concentrations exist. The bromine is chemically displaced by chlorine, which replaces it in the bromides. It is then extracted by organic solvents.

Iodine was discovered in the ashes of seaweed by the French chemist Bernard Courtois in 1811. Iodine does not exist in the free state, but only in chemical combination. It is extracted from iodides by means of sulfuric acid and an oxidiz-

DIP FUNNEL—This funnel contains bromine, which is poured drop by drop into a reaction flask. Bromine, a liquid at room temperature, evaporates readily to produce a vapor (the red vapor in the top of the funnel).

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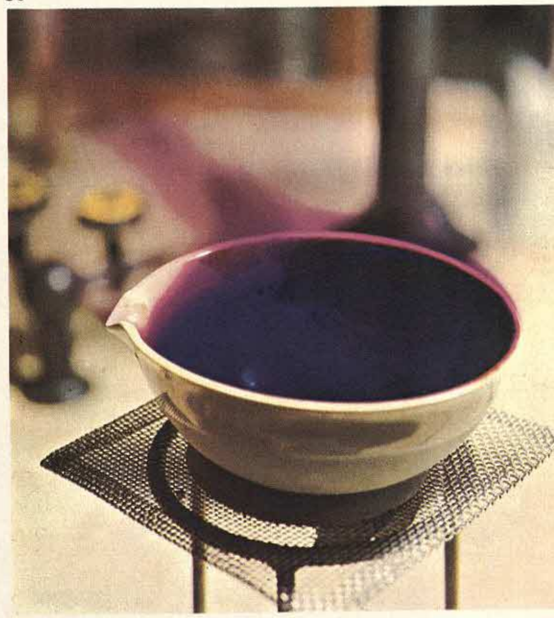
3a

3b

3c



IODINE — Unlike bromine, this element is solid at room temperature. It occurs in the form of dark crystals with a metallic luster (Illustration 3a). It sublimes easily (Illustration 3b) and is volatile, forming extremely irritating violet vapors (Illustration 3c).

ing agent such as manganese (IV) oxide. The iodine is then extracted with paraffin. It is separated from the paraffin by heating with a solution of sodium sulfite in the presence of sodium hydroxide. It can be extracted also from iodates by heating these salts with sodium bisulfite. This produces free iodine and some iodide, which can be precipitated as copper(I) iodide.

Astatine was first prepared in 1940 by bombarding bismuth-209 nuclei with alpha particles. A bismuth nucleus absorbs an alpha particle, but then immediately expels two neutrons by radioactive decay, thus changing into astatine-211. This isotope is unstable and has a half-life of about 7.23 hrs (that is, it decays by halving the number of radioactive atoms present in 7.23 hrs). Because of this high rate of decay, the element was called astatine, which means "unstable."

Seventeen istotopes of astatine have been prepared in a similar manner. Except for astatine-210, all are more unstable than astatine-211.

PROPERTIES OF THE ELEMENTS

Bromine is the only nonmetallic element that exists in liquid form at room temperature. It has a very low viscosity and is red-brown in color. At room temperature, bromine evaporates to form a red-brown vapor; the vapor is very irritating to the eyes and throat. Bromine has an odor similar to that of chlorine. At room temperature, it dissolves in water to form a 2.55 percent by weight solution called bromine water. If potassium bromide is present, the solubility of bromine increases as a result of the formation of polybromides.

Many organic solvents, such as carbon disulfide, dissolve bromine readily. Its greater solubility in organic solvents provides a method for extracting it from aqueous solutions. At room temperature, the density of liquid bromine is more than three times the density of water. Its vapor is also quite dense, about six times the density of air.

At normal temperature and pressure, iodine is a solid in the form of dark, scaly crystals. These crystals are purplish-black with a metallic luster. Iodine, like bromine, is volatile and sublimes to form blue-violet vapors that have an unpleasant odor and irritate the eyes and throat. Because of its lower chemical reactivity, iodine is less caustic than bromine and chlorine, and does not produce burns as quickly when it comes into contact with the skin. Iodine vapors are about eight times as dense as air. The amount of iodine by weight that dissolves in water is only 0.015 percent. Even this low percentage is sufficient to produce a yellowish coloring in the solution. Iodine also dissolves readily in many organic solvents such as alcohol, chloroform, ether, carbon tetrachloride, and carbon disulfide.

USES

Bromine and iodine, both in the elementary state and in compounds, are used in a number of important industrial and laboratory applications.

The most important application of bromine, one in which it is practically irreplaceable, is in photographic emulsions. The substance that darkens photographic film is silver bromide. In general, bromine compounds are synthesized by direct contact with the appropriate elements. For this reason, extraction processes yield the elementary form of the element.

Among the important bromine compounds are certain bromides that produce a calming effect on the nervous system. Whole sea salt, which contains all the salts in seawater, including bromides, is a mild tranquilizer. Many bromine compounds are important in the synthesis of organic substances. Ethylene dibromide is a volatile substance used as

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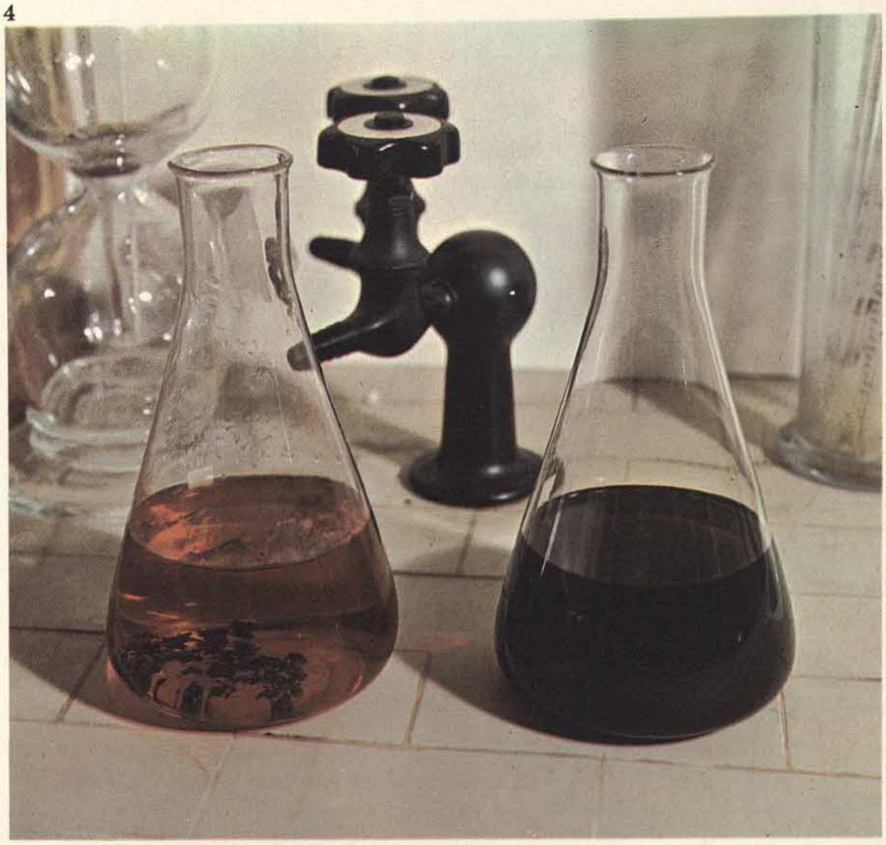

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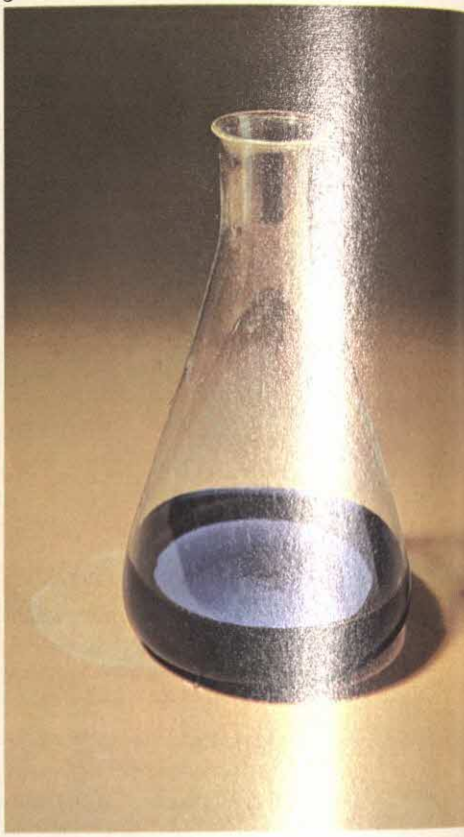


IODINE IN SOLUTION—Iodine is only slightly soluble in water, although it dissolves to produce a yellow-reddish color—as in the left-hand flask. In organic solvents, on the other hand, iodine is extremely soluble. As a result, such solutions are highly colored. The right-hand flask contains a solution of iodine in alcohol—a solution known as tincture of iodine.

IODINE AND STARCH—Iodine colors starch dark blue. This property is used as a test for the presence of starch in organic substances, and also for certain volumetric analyses.

a lead scavenger in an antiknock agent in gasoline. Large quantities are produced for this purpose.

Iodine occurs widely in small quantities in biological tissues, and in the thyroxin of the thyroid gland. A deficiency of the element causes goiter; this deficiency is usually due to a lack of iodine in the water and occurs frequently in certain mountain and inland regions. The usual remedy is table salt containing iodide salts.

An iodine solution in alcohol (tincture of iodine) is used as an antiseptic. Silver iodide is used in small quantities in photography together with silver bromide. Iodine colors starch blue, thus providing a test that reveals the presence of starch in organic substances or biological tissues. It is more important, however, in volumetric analysis for certain titrations; such analysis is called iodometric analysis. Iodine compounds are employed in other analytical procedures.

CHEMICAL PROPERTIES

Bromine and gaseous iodine form covalent diatomic molecules that dissociate only at high temperatures or in the presence of ultraviolet radiation. The chemical properties of the halogens vary gradually from fluorine to iodine. In fact, fluorine is the most electronegative of the halogen elements. The electronegativity of iodine, however, is comparable to that of hydrogen.

Bromine and iodine are both less reactive than fluorine or chlorine, although they both attack the noble metals with great ease.

With respect to oxidation states, fluorine usually has a valence of -1 (very exceptionally, -2). Chlorine and iodine, however, have oxidation states varying from -1 to $+7$, while bromine has values of -1 to $+5$.

Hydrogen bromide, HBr, and hydrogen iodide, HI, are covalent substances that are volatile and quite soluble in water. In aqueous solution they behave as strong acids (in other words, they ionize into H^+ and X^-). Hydrofluoric acid, however, is a weak acid. Since bromine and iodine are much less electronegative than fluorine or chlorine, they may react with fluorine or chlorine to produce interesting compounds such as $Br^{(+)}Cl^{(-)}$ and $I^{(+)}Cl^{(-)}$. In these compounds the anion is provided by the more electronegative element.

Among the oxygenated bromine salts are sodium hypobromite, NaBrO, and sodium bromate, $NaBrO_3$. The oxidation state of bromine in NaBrO is $+1$; in $NaBrO_3$ it is $+5$. The chemically and industrially important oxygenated iodine salts are sodium iodate, $NaIO_3$, and sodium periodate, $NaIO_4$. The oxidatation state of iodine in $NaIO_3$ is $+5$; in $NaIO_4$ it is $+7$.

In solution, iodine can form bases and act as a metal in some salts.

THE NOBLE GASES | helium, neon, argon, krypton, xenon, and radon

The atoms of most of the elements are most stable when they have eight electrons in the outermost energy level. This state is usually achieved by entering into chemical bonds with other atoms. Chemical affinity—that is, the readiness of an element to react with other elements to form compounds—is due precisely to this tendency to achieve the lowest energy state and the greatest stability possible.

The atoms of some naturally occurring elements, however, already have their outer energy levels saturated with electrons. These atoms, therefore, do not react readily with other atoms. Such elements are said to be chemically inert. This explains why these atoms are found in the gaseous state. Moreover, while all other gaseous elements occur at room temperature as diatomic molecules (with each atom in the molecule having an octet of outer electrons), the noble gases occur as monatomic molecules. That is, each atom is by itself the smallest particle that displays the characteristics of the element (this is the definition of a molecule).

The reluctance of atoms of these elements to unite with other atoms has led to the name "noble gases." Six such noble gases exist: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn); all have similar properties. Apart from a considerable chemical inertness, they liquefy at extremely low temperatures. The heavier elements in the group are the first to liquefy because thermal agitation of the atoms at any given temperature is always less if the atom is heavier. Atoms of the noble gases are in the gaseous state because thermal agitation overcomes the short-range forces of attraction that come into play at every collision. When the temperature falls, however, the agitation also decreases; eventually it becomes so insignificant that it is no longer able to oppose the attractive forces between atoms. At this point the colliding atoms are no longer able to rebound away from each other and the gas condenses into a liquid.

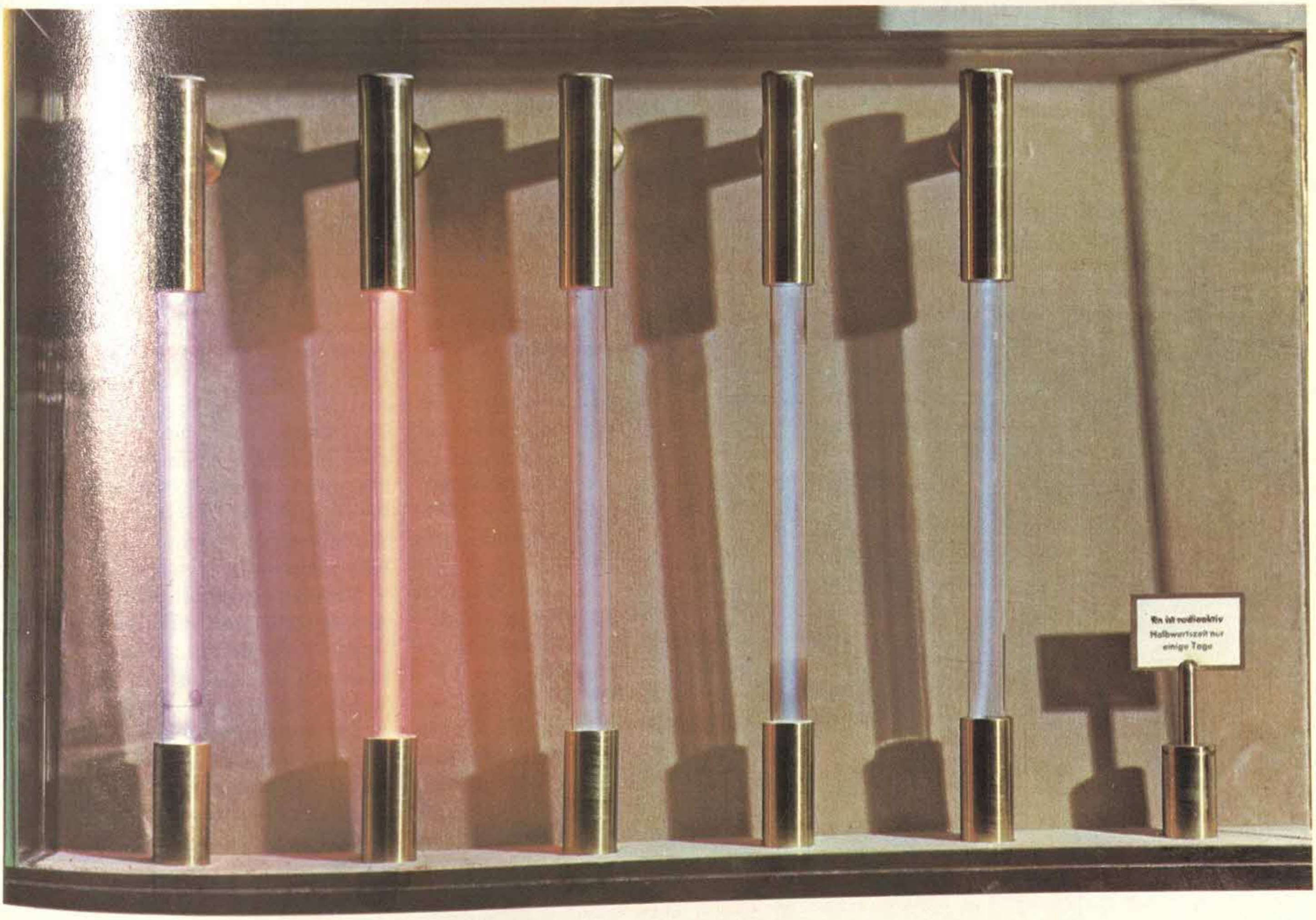
Until recently, almost complete chemical inertness was attributed to these elements. It is now known, however, that they form some rather stable compounds.

WHERE NOBLE GASES ARE FOUND

The noble gases are found in the free state in the atmosphere. Some of them are continually being formed as a result of radioactive decay.

Helium is formed when an alpha particle (a helium nucleus consisting of two protons and two neutrons) captures two electrons to match its two protons. The most common radioactive elements in the Earth's crust—uranium and thorium

THE FAMILY OF NOBLE GASES—This photograph shows all the noble gases and their characteristic discharge color. Quite low voltages are sufficient to produce these luminous discharges. The last place on the right belongs to radon. This gas is radioactive, however, and quickly decays, first into polonium and then into lead. The label in German reads "Rn is radioactive with a half-life of only a few days."



–produce alpha particles and, therefore, helium during radioactive decay. Each disintegration produces an alpha particle, which becomes a free helium atom once it has picked up two electrons.

Most helium atoms remain imprisoned in the rocks within which they were produced. Nevertheless, a few find their way through the pores of the rock and eventually escape into the atmosphere. Helium produced by radioactivity of lavas (which solidify into igneous rock) has a greater probability of escaping because it bubbles through the fluid magma with comparative ease. The helium that finds its way into the atmosphere eventually escapes into space. Because atoms of helium are extremely light, they acquire speed as they diffuse into the upper atmosphere and on into space. If all the helium produced by radioactive decay in the Earth's crust remained in the atmosphere, the atmosphere itself would today consist primarily of this gas. In actuality, helium is found in the atmosphere in minimal quantities only.

Some minerals—cleveite for example—contain helium trapped within their crystalline lattices. In such cases, the gas can be freed by heating the mineral. Helium can also be obtained from radioactive decay reactions. Nevertheless, the main sources of the element are North American natural gas deposits.

Neon, argon, krypton, and xenon are found in the atmosphere, generally in very low concentrations. The only exception to this rule is argon, which accounts for as much as 0.94 percent of the atmosphere by weight. Neon, krypton, and xenon, on the other hand, account for only 0.0012 percent, 0.0003 percent, and 0.00004 percent of the atmosphere, respectively.

Radon has no stable isotopes. All of the radon existing in nature is radioactive; it is, therefore, destined to disappear by radioactive decay. In fact, radon would not be found on Earth at all if it were not for the fact that it is continually produced by the radioactive decay of radium. Radon is thus similar to helium; that is, it is present in the atmosphere in minimal quantities only because it is continually supplied by the disintegration of radioactive elements. Helium is lost because it escapes from the atmosphere, while radon decays and is transformed into other elements.

DISCOVERY OF THE NOBLE GASES

When the English chemist and physicist Henry Cavendish tried in 1785 to separate first oxygen and then nitrogen from the air, he found that about one part in 120 appeared to consist of a third gas that was chemically inert. In reality, this inert fraction, argon, is somewhat larger; it amounts to almost one eightieth of the mass of atmospheric air. In 1894 the isolation of argon was accomplished by the English physicist Lord Rayleigh and the Scottish chemist William Ramsey.

Somewhat later, in 1898, Ramsey experimented with the fractional distillation of air. After separating oxygen, nitrogen, and argon, he also succeeded in isolating neon, krypton, and xenon. Neon was the most volatile of these three gases, while krypton and xenon were the most readily liquefied.

Helium was discovered under rather curious circumstances. Indeed, it was discovered in the sun before it was actually found on Earth. Using spectroscopy, the French astronomer Pierre Janssen revealed in 1868 that the solar spectrum contained a yellow line that could not be reproduced in the laboratory by exciting (with flames or sparks) any element then known. Suspecting that this line must be produced by some new element, astronomers suggested that it should be given the sun's Greek name (*helios*). Ramsey then succeeded (1895) in isolating an appreciable quantity of helium, which he extracted from a mineral containing uranium.

THE PROPERTIES OF HELIUM

Next to hydrogen, helium has the lowest specific gravity of all elements. It is used for inflating balloons and dirigibles because it is not flammable and will not explode. It is the most difficult of all the gases to liquefy; that is, its liquefaction temperature is the lowest known. At atmospheric pressure the gas liquefies at −268.9° C (about −452° F). This is only a few degrees above absolute zero. At ordinary pressure (one atmosphere), helium does not solidify at any temperature, no matter how low. In 1926 helium was solidified by cooling it to −272.2° C (about −458° F) under a pressure of 26 atmospheres.

At temperatures below 4.2° K (about −452° F) liquid helium has some rather exceptional properties. When cooled, the gas maintains its normal properties down to 2.9° K (about −454° F). In this range it is called helium I. Below 2.9° K, however, some of its properties become quite strange. For example, the gas expands as the temperature diminishes; the specific heat (the amount of heat needed to increase the temperature of 1 g of the substance by 1° C) increases by a factor of ten over a small range of temperature; when the temperature is lowered still further, the specific heat becomes quite small indeed.

Helium displaying these anomalous properties is known as helium II. Liquid helium in this phase rises up the walls of a tube immersed in it, even when the diameter of the tube is not of capillary dimensions. The thermal conductivity of helium II is extremely high—infinite for all practical purposes. This means that if a mass of helium is heated at one particular point, the heat will be distributed almost instantaneously throughout the entire mass.

USES OF THE NOBLE GASES

Helium is used for discovering losses from vacuum chambers; for refrigerating the cores of nuclear reactors and transferring the heat to a place where it can be utilized; for maintaining a constant pressure in the fuel tanks of missiles as the fuel diminishes; for maintaining metallic surfaces in an inert atmosphere while they are being heated during welding operations, thus preventing oxidation; for inflating balloons; and for preparing breathing mixtures for deep-sea divers.

Argon is often used in place of helium for protecting metals during welding. It is sometimes used to produce an inert atmosphere for the smelting of metals that would oxidize if exposed to air at high temperatures. Argon is also used in a medium-power, continuous wave laser that is employed in spectroscopy and communications.

Neon signs depend on the beautiful orange-red light the gas emits when an electric discharge passes through it. The light takes on other color tones if small quantities of other gases are added. This use, however, is less important today because fluorescent lamps are more economical to operate than are neon lamps. The electric discharge in neon is also used in voltage stabilizer tubes. Neon, along with helium, provides the supporting medium for the helium-neon laser, the least expensive and most commonly used laser.

The most important use of xenon is in photographic flashbulbs. If an electric discharge is passed through xenon, an extremely intense white light is produced. This light is most suitable for both taking and projecting color photographs. The light yield of xenon and neon discharges is particularly high; it may be five times as great as that of a filament bulb. This xenon-neon light yield is used in spectroscopy.

Up to the present time, neither krypton nor radon has important applications.

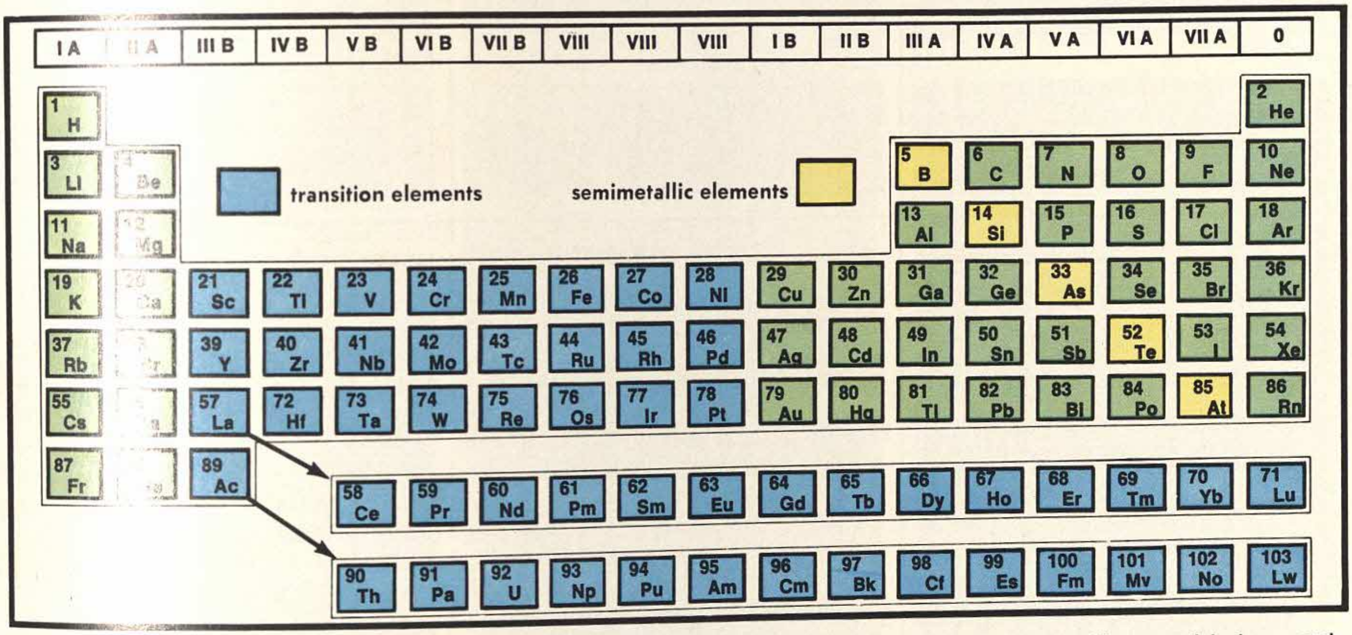
ALKALI METALS AND ALKALINE-EARTH METALS

The periodic table is chemistry's fundamental filing system. It lists each of the more than 100 known elements in such a precise way that a thorough understanding of the table is basic to any study of the chemical and physical properties of matter. Illustration 1 shows a generally accepted layout of the periodic table.

In Group IA of the table, the six elements following hydrogen are the alkali metals: lithium, sodium, potassium, rubidium, cesium, and francium. The word *alkali* is derived from the Arabic for saltwort ashes. (In fact, sodium and potassium carbonates are abundant in plant ashes.) To the chemist, *metal* is a general word defining materials that conduct heat and electricity well; that have a characteristic luster; and, in general, are malleable. The alkali metals possess these physical properties.

All elements in the alkali-metal group share other characteristics. For example, each has a single electron in its outermost shell. Furthermore, these elements are assigned two values for their respective ionization potentials. The first value is the amount of energy required to remove the single valence electron; the other specifies the energy needed to remove a second electron. The first constant is relatively low, because it is "easier" to give up one electron than to acquire enough new ones to completely fill the outermost shell. On the other hand, because the next-to-outermost shell of these atoms is filled to capacity, the second value is very high, and a great deal of energy is required to displace an electron. Simply, this means that the alkali-metal group yields ions with a +1 oxidation-number and that it is virtually impossible to produce +2 ions.

For the alkali metals, and for other metals as well, heat and electrical conductivity are properties related to the formation of a cubic crystalline structure. Using the symbol Me to stand for a metal ion, and Me^+ for a metal ion with a +1 charge, one may say that the Me^+ ions occupy positions at the vertices and center of the cube's structure, or lattice. The metal's valence electrons, one for each atom, comprise the "atmosphere" of the lattice. These electrons have complete freedom of movement within the lattice in contrast to the ions and their fixed positions. When a crystal of this type is subjected to an electric field, the electrons move in the direction of the positive electrical influence. The result is a flow of negative charge through the



PERIODIC TABLE OF THE ELEMENTS— Chemistry's organization chart as shown here is the modern progeny of the nineteenth-century Russian scholar Dmitri Mendeleev, who first recognized the ordered relationship of the elements. His original periodic table listed the 58 elements known at that time, and left gaps for seven others, whose existence he correctly predicted. The table now lists all the known elements according to their atomic number. Those elements shown in green squares are considered metals or nonmetals. The transition elements, exhibiting some properties of both the metals and nonmetals, are shown in blue, while a special class, semimetals, is shown in yellow squares. The two separate series of elements at the bottom of the illustration are the lanthanide series (atomic numbers 58 through 71) and the actinide series (atomic numbers 90 through 103).

crystal, which explains why metals are good electrical conductors.

Within the crystal, however, are forces opposing the electron migration. These forces are created by the ions vibrating around, but not leaving, their fixed positions in the lattice. This resistance to electron movement tends to counteract the high kinetic energy of the valence electrons.

If the temperature of the crystal lattice is increased by some outside source, a corresponding increase in the frequency of ion vibration occurs. The speeding up of the ion motion heightens the internal resistance to electron movement, which accounts for decreased electrical conductivity in metals at increased temperatures.

A metal can be classified as either a good or poor conductor of heat for the very same reasons it does or does not conduct electricity. Both these properties rely on the movement of electrons within the crystal lattice.

The periodic table in Illustration 1 shows each element and its corresponding atomic number starting from one. As the atomic number increases, the number of electrons in each successive element increases. In order to chart each element's electrons, a system has been devised that assigns an electron configuration to the elements. This system uses the letters K through Q to denote electron shells, each shell containing a definite number of electrons.

In the case of the alkali metals, then, it is logical to assume a regular increase in the size of their respective ions as the number of electrons in each increases. For example, the first two elements in this series, lithium and sodium, each have the same valence (oxidation number), but differ considerably in ion size. With lithium, Li^+, only the K shell is occupied. Sodium's ion, Na^+, has the K and L shells filled with electrons. Thus, the radius of the sodium ion is greater than that of the lithium ion.

An increase in the size of an atom and in its associated ion means a greater distance between the nucleus and the outer

2

ALKALI METALS—Group IA in the periodic table of the elements contains the alkali metals. The characteristics of this group are a single valence-electron and good heat and electrical conductivity. The first element in this series is lithium, with an atomic number of 3 (Illustration 2a). Next come sodium (Illustration 2b), potassium (Illustration 2c), rubidium (Illustration 2d), and, not illustrated, cesium and francium.

3

BERYLLIUM AND MAGNESIUM — Beryllium (Illustration 3a) and magnesium (Illustration 3b) are two representatives of the alkaline-earth metals from Group IIA in the periodic table. Because these elements have two valence-electrons, they produce bivalent ions. In nature, beryllium is responsible for one of the most beautiful of gems, the emerald. Magnesium is the lightest known structural metal in the world.

electrons with a corresponding decrease in the forces that bind the valence electron to the atom; this indicates a relationship to ionization potential. In fact, ionization potential decreases inversely to the radius of the atom. The larger the atom, the less energy needed for ionization.

A chemical property common to the alkali metals is their great power to act as reducing agents. Because this extreme reactivity causes handling and storage problems the alkali metals are generally stored immersed in an inert petroleum product such as kerosene. Even brief contact with the moisture in air oxidizes these substances. Exposed to water, the alkali metals can react with explosive violence according to the following reaction:

$$2Me + 2H_2O \rightarrow 2Me^+OH^- + H_2.$$

The next group in the periodic table, Group IIA, includes beryllium, magnesium, calcium, strontium, barium, and radium—the alkaline-earth metals. These elements each have two electrons in their outermost shell, forming ions of the Me^{2+} type. The elements in Group IIA do not form Me^+ ions because such ions are unstable in solution. Recent theories state that monovalent ions in this group change into the stable bivalent ions through a process of dismutation, or auto-oxidation-reduction. This is a somewhat complex process of oxidation and reduction within the ions. Simply, two Me^+ ions oxidize to a single Me^{2+} ion and a neutral Me atom is concurrently formed through reduction.

Like those in Group IA, the alkaline-earth elements possess metallic properties. However, they are harder than the alkali metals and have higher melting and boiling points. The higher boiling points indicate stronger binding forces between Me^{2+} ions and the electron atmosphere than in the Group IA metals. Alkaline-earth metals occur most often in the form of carbonates and sulfates.

As with the alkali metals, there is a consistent increase in atomic size paralleled by a decrease of ionization potential in the alkaline earths. An interesting difference, however, is the smaller size of the atoms and ions of the Group IIA elements. For example, both potassium and calcium have complements of two

4a

4b

4c

4d

ALKALINE-EARTH METALS — The remaining members of Group IIA are shown here. These elements, along with beryllium and magnesium, differ from the alkali metals not only in oxidation number, but they also exhibit lower heat and electrical conductivity and have smaller atoms than the IA elements. Calcium (Illustration 4a) is important for proper bone and tooth formation. The other family members are strontium (Illustration 4b), barium (Illustration 4c), and radium (Illustration 4d).

electrons in the K shell, eight L-electrons, and eight M-electrons in the ionic state. What, then, accounts for the difference in radii? It is due to the fact that the charge on the nucleus is greater for calcium than for potassium. For this reason, the K, L, and M shells in the calcium ion are more "condensed," with a greater force pulling the electrons toward the nucleus.

The smaller size of the Group IIA ions also accounts for the greater ionization potentials of the alkaline-earth elements. The smaller volume that creates stronger binding forces between the nucleus and the electrons requires greater energy to remove electrons in ion formation.

Like the alkali metals, the alkaline-earth elements exhibit strong reducing properties but to a lesser degree. Although more energy is required to ionize the IIA metals, they react violently with water molecules during hydration. It is more accurate, therefore, to use the term *hydration energy* when referring to the alkaline-earth metals as reducing agents.

CARBON | diamonds, lubricants, and drills

When man first "discovered" the element carbon (C) may never be known because instances of its early use are shrouded in prehistory. The fact remains, however, that carbon is the most important element on Earth and, by extension, in the universe. Without carbon there would be no basis for either plant or animal life. The energy of the sun and stars is due in part to the carbon-nitrogen cycle, and carbon is found (by spectrographic analysis) in the atmospheres of most planets.

Although not the most widely distributed substance, carbon and its compounds form the largest group of substances: the organic compounds. These, and the inorganic matter of which carbon is a part, account for millions of different substances. Underlying this is the unique ability of carbon to form compounds in which carbon atoms are joined to one another. A simple example of this ability is starch triacetate, a single molecule of which contains 216 carbon atoms.

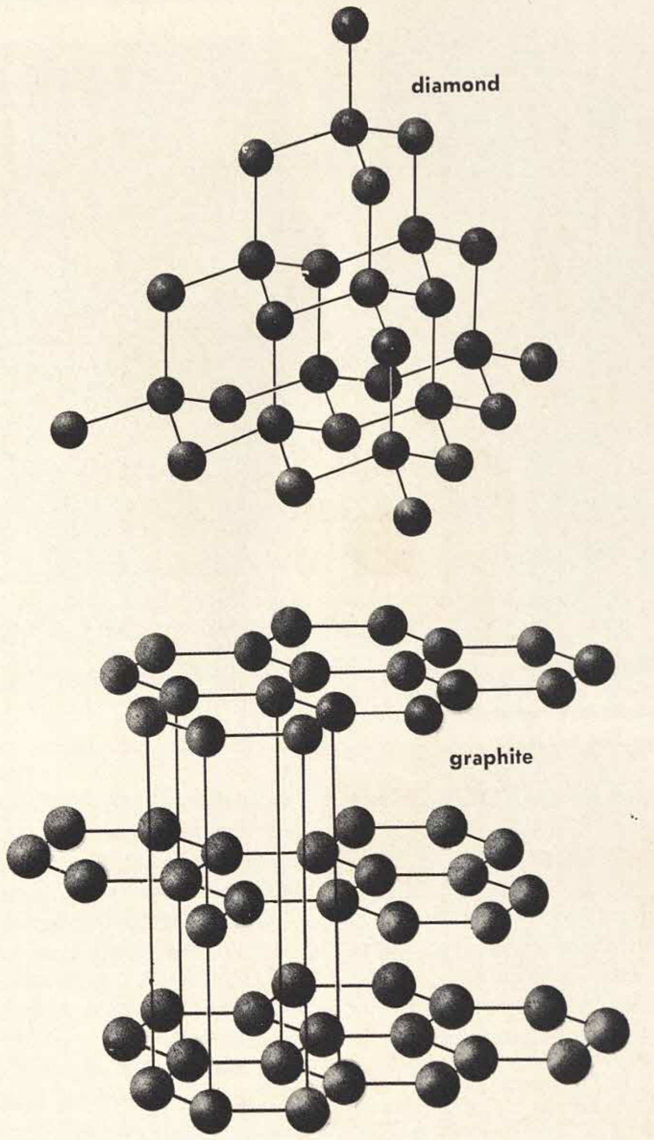
Carbon-carbon bonds are characteristic of organic matter, but carbon also forms multiple bonds with other elements of the periodic table to yield compounds such as carbon dioxide (CO_2), carbon disulfide (CS_2) and carbon diselenide (CSe_2). In these examples, a typical oxidation state of +4 is exhibited. Certain compounds demonstrate a +2 valence, as with carbon monoxide (CO), the lethal product of incomplete fuel combustion.

In the elementary state, carbon exists in any of three allotropic forms: amorphous carbon, graphite, and diamond. Among these are one of the softest and one of the hardest materials known: graphite and diamond, respectively.

DIAMOND AND GRAPHITE—Here, in structural representation, are carbon's two crystalline allotropes. The first is diamond (Illustration 1a), a complex series of tetrahedrons whose vertices are occupied by carbon atoms. This structure is extremely rigid in all directions. Graphite (Illustration 1b), on the other hand, is shown in its characteristic lamellate configuration. This series of stratified hexagons, one above the other, is held together by weak electrostatic forces (known as Van der Waals forces). The weakness of these bonds allows slippage between planes, accounting for graphite's softness and greasy feel.

1a

1b



NATURAL DISTRIBUTION OF "INORGANIC" CARBON

In the Earth's crust, carbon as a component of minerals occurs primarily in the carbonates of calcium, magnesium, and iron. As an uncombined element, carbon is found as diamond, although the distribution is considerably less than that of carbon compounds.

The atmosphere contains a small amount of carbon in the form of carbon dioxide. While this gas makes up about 0.03 percent by volume of the total atmosphere, it represents the primary carbon source for all living organisms. In particular, the existence of plants depends on the assimilation of atmospheric carbon dioxide to produce carbohydrates through photosynthesis. This represents the first step in the so-called biological cycle. Through a series of events, the plants provide nutrition to animals and man with the cycle completed when carbon dioxide is returned to the atmosphere as a waste product.

2a

2b

AMORPHOUS CARBON—Carbon black (Illustration 2a) is pure carbon obtained from burning hydrocarbons, and is used extensively in the rubber industry. The charcoal in Illustration 2b is a product of the incomplete combustion of wood. Both forms of amorphous carbon can be used for purification through adsorption.

The vast quantities of carbon in coal and oil deposits bear witness to the millions of years that vegetable matter has been assimilating carbon dioxide.

DIAMOND, GRAPHITE, AND AMORPHOUS CARBON

Of the three forms of elementary carbon, only diamond and graphite have crystal structures. Amorphous carbon is essentially a haphazard arrangement of carbon atoms, although x-ray studies have shown that some of these atoms do arrange themselves in a manner not unlike graphite. In fact, heating amorphous carbon above 1,000° C (1,832° F) causes the atoms to rearrange themselves into a true graphite lattice. This process, called graphitization, is used to manufacture synthetic graphite.

Aside from its conversion to graphite, amorphous carbon is used as a pigment and dye. More important, perhaps, is the material's use as activated charcoal, where its ability to adsorb gases is exploited. This property makes amorphous carbon invaluable for purifying liquids; when the amorphous carbon is cooled to very low temperatures, it is used to remove residual gas molecules in vacuum pumping operations.

Graphite is extensively used to make carbon electrodes for the metallurgical industries, specialized electrolytic cells, and foundry molds. For the most part, these applications require graphite of only moderate purity, which can be obtained by the graphitization of petroleum pitches. Extreme purity is of utmost importance, however, when graphite is used as a moderator in nuclear reactors. In this instance, impurities of boron in excess of one part per million and of certain rare earths in excess of one part per billion are unacceptable. Graphite meeting these requirements is obtained by first removing impurities before graphitization.

Structurally, graphite crystals resemble flat scales lying in planes one above the other, much like a neatly stacked pile of bricks. This structure allows each plane to slip readily in a horizontal direction with respect to adjoining planes. It is this property that gives graphite its characteristic greasy feeling, and that makes it an excellent lubricant, especially in applications where liquid compounds would freeze or cause sticking. Another physical property that has practical application is graphite's coefficient of expansion. This is almost identical to that of certain metals, especially zirconium, and several alloys. This allows welding of the dissimilar materials to make specialized equipment.

At some point between the crystal structure of ordinary graphite and that of diamond occurs a modification in atomic arrangement that produces graphite that is extremely hard and almost as impermeable to gases as is glass. This form of the substance is also highly resistant to corrosion and high-temperature failure. As such, this type of graphite is used in high-temperature nuclear reactors. More important, perhaps, is its use in exhaust nozzles of rocket engines where its integrity remains even at temperatures approaching 3,000° C (5,432° F).

3a

3b

3c

DIAMOND—Another form of pure carbon, diamond is used both for jewelry and for making industrial cutting tools. Its extreme hardness allows diamond tools to cut materials that would quickly ruin the cutting edges of conventional equipment. The illustrations show diamond in three forms: single crystals (Illustration 3a), a rough-textured powder (Illustration 3b), and as a finely divided powder (Illustration 3c).

The third modification of carbon, diamond, is the hardest natural substance known. The extent of its hardness is due entirely to a crystalline structure that is equally rigid in all directions. Unlike graphite, considerable force is required to alter the crystalline configuration.

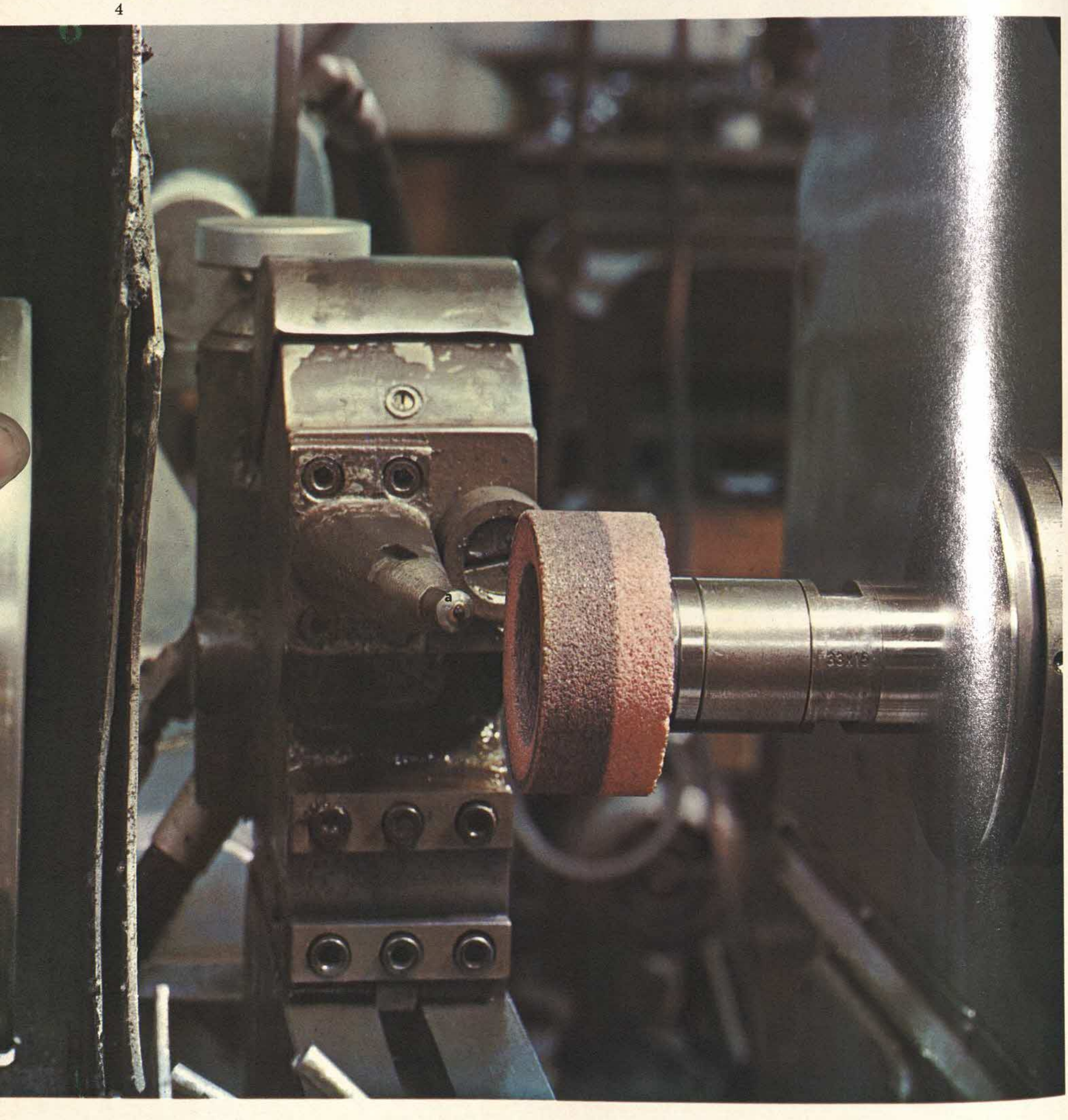
Diamond is the most valuable form of carbon, not only from the standpoint of the jeweler's showcase, but for industry. Its extreme hardness allows its use in

5

DIAMOND-STUDDED CORE DRILL—The tips of drills used in prospecting for oil must be able to penetrate layers of hard, subsurface rock. To prevent the diamonds in this drill from conversion to graphite, the rig is cooled below 1,000° C (1,832° F).

REFINISHING A GRINDING WHEEL WITH DIAMOND—Each time a grinding wheel is used, the particles of metal it rubs off lessen its abrasive properties. The diamond-tipped tool **a** is used to refinish the wheel's surface, renewing its usefulness.

4

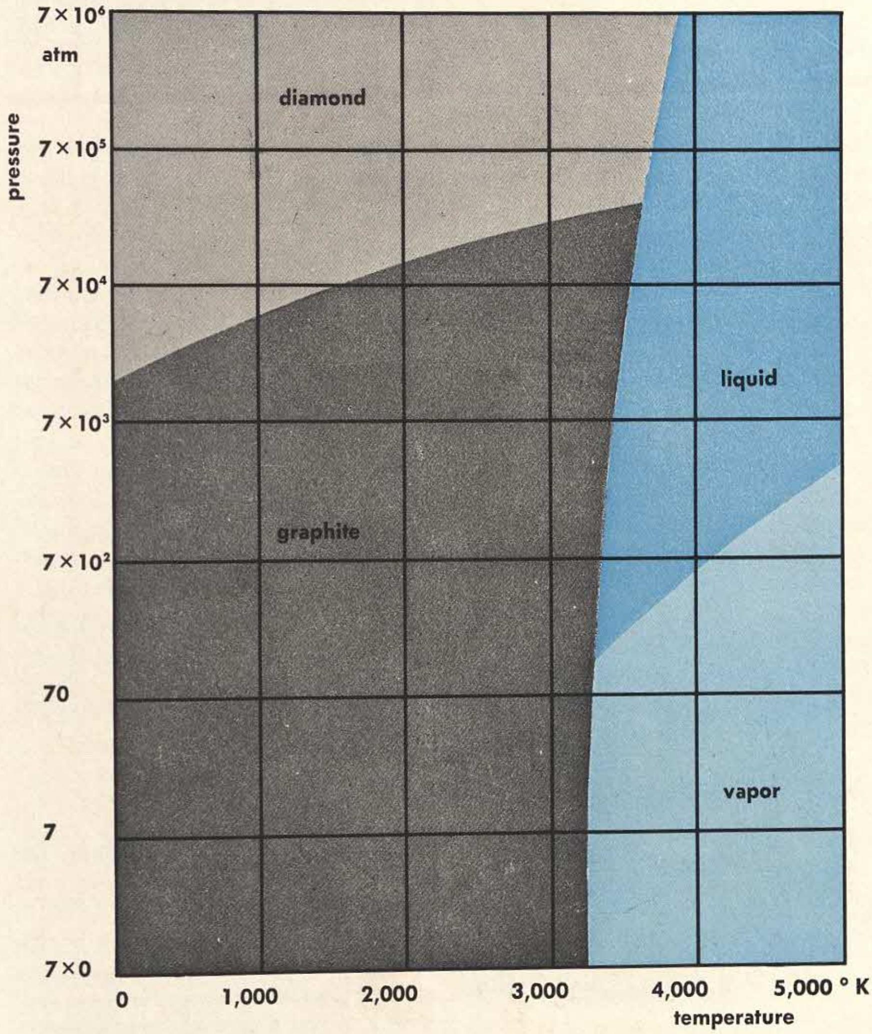


cutting tools that will slice through almost any material. Diamond is used for special grinding wheels, and for tipping drilling tools. In the latter case, diamond-tipped bits able to cut through layers of hard rock are used by the oil industry. However, in any high-speed cutting, grinding, or drilling operation that incorporates diamond, care must be taken that the heat created by friction does not exceed 1,000° C (1,832° F). At about this temperature diamond converts to graphite.

Diamonds occur in nature in the form of octahedrons and 48-faced hexoctahedrons. Those that have pure, subtle hues or are completely transparent are destined for jewelry. Others that are less desirable become industrial diamonds. In fact, the impurities contained in less-than-gem quality stones enhance the hardness factor.

The story of creating artificial diamonds from graphite began in the nineteenth century, when the French chemist Henri Moissan successfully obtained minute stones of highly inferior quality. The technique in performing such a transmutation is the duplication of natural processes. In nature, diamond is created deep in the Earth over long periods of time by a combination of heat and intense pressure. In the process, graphite-bearing volcanic magma is converted into diamond. Quite expectedly, the richest diamond deposits are found in the ducts of long-extinct volcanoes, and such deposits have yielded gems of incredible size and purity, such as the 3,106-carat Cullinan diamond, the world's largest known gem diamond, and the recently discovered Sesotho diamond, a 601-carat stone valued at $850,000 uncut.

Since Moissan's time, techniques have been developed that mimic nature. Industry is now capable of producing the high temperatures and pressures required to transform graphite to diamonds of commercial quality. In the course of this research, the graphite-diamond phase diagram was developed, and this clearly explains the formation of graphite and diamond with respect to pressure. It has been determined, also, that certain materials (primarily chromium) act as catalysts able to convert graphite to diamond at temperatures approaching 2,000° C (3,632° F) under a pressure of 100,000 atmospheres. This is equivalent to conditions in the Earth at a depth of 32 km (about 20 mi). Before the discovery of such catalytic agents, a temperature and pressure twice as high was required. Although the cost of synthetic industrial diamonds is somewhat higher than that of the natural product, the quantity is not limited as is the case with natural diamonds.



CARBON PHASE DIAGRAM—The research that led to the successful synthetic conversion of graphite into diamond has resulted in this diagram that illustrates several transformation thresholds of carbon as functions of temperature and pressure.

ACTINIUM, THORIUM, AND PROTACTINIUM | elements in the actinide series

The series of elements in the actinide series ends the periodic table as it is now known. These metals begin with actinium (atomic number 89) and traverse the natural elements through uranium (92) into the man-made atoms from neptunium (93) to lawrencium (103). The eleven final elements in this series are also called the "transuranium" metals; these elements are never found in nature.

While a great deal is known about the nuclear properties of elements 93 to 103, little or nothing is known about their chemical or physical properties. Since all the actinide metals are radioactive, they have extremely short lifetimes, decaying through the emission of either alpha particles (helium nuclei), beta particles (high-speed electrons), or gamma rays. As a secondary effect, x-rays are sometimes emitted.

1a

1b

TWO IMPORTANT MINERALS—One ton of pitchblende, such as that in Illustration 1a, yields about 0.15 mg (about 0.0005 oz) of actinium. The monazite in Illustration 1b is a thorium ore containing from 3 to 9 percent thorium oxide.

When an element decays by emitting an alpha particle, its mass is decreased by two atomic mass units, with a corresponding lessening of the nuclear charge. Thus, the element becomes an isotope of the matter preceding it by two atomic numbers; for example, uranium-238 is transformed into an isotope of thorium-234. The emission of a beta particle, on the other hand, makes no appreciable difference in the mass; however, the nuclear charge is increased by one unit, creating an isotope of the following element. Uranium (atomic number 92), for example, becomes an isotope of neptunium (atomic number 93).

ACTINIUM

Actinium was discovered in 1899 by the French chemist A. L. Debierne as a residual product of uranium ores. Later, in 1902, F. O. Giesel independently discovered the element mixed with rare earths in pitchblende. In the years following, it was determined that actinium belonged to a series of radioactive elements derived from uranium-235.

Only the actinium isotopes actinium-227 and actinium-228 occur naturally. However, many others can be produced from thorium, uranium, and radium by bombarding them with nuclear particles. Because the half-life of actinium-227 is only 22 years, it would be impossible to find the element in nature were it not continually re-created from isotopes preceding it in the series.

Actinium, a silvery-white metal, is the second rarest element in nature; the material from which it is created, ^{235}U, accounts for only 0.71 percent of native uranium. In fact, one ton of pitchblende yields on the order of 0.15 mg (about 0.0005 oz) of the material. Because the concentrations of actinium are very small, and because its chemical properties appear to ape those of lanthanum, it is difficult to extract the element from its sources. Ion-exchange processes can be used to separate actinium and lanthanum, although very minute quantities of actinium are produced. More efficiently, a nuclear reactor utilizing radium and high-speed neutrons can produce the element in usable proportions. This synthesis was first achieved by Peterson in 1945, according to the reaction:

$$^{226}\mathrm{Ra} + \mathrm{n} \rightarrow {}^{227}\mathrm{Ra} + \gamma \xrightarrow{42\ \mathrm{min.}} {}^{227}\mathrm{Ac} + \beta.$$

The radium absorbs a neutron and converts to the very unstable ^{227}Ra isotope that emits a gamma ray. With a half-life of 42 minutes, this isotope produces actinium-227 by emitting a beta particle.

The melting point of actinium is 1,050° C (1,922° F); the boiling point is estimated to be 3,200° C ±300° (about 5,792° F ±500°). Actinium always produces trivalent compounds and its chemistry is similar to that of lanthanum. It combines with all the halogens and forms a hydroxide, an oxalate, an oxide, and a sulfide. In quantities exceeding a milligram, actinium is difficult to handle because of the intense radiation developed by its decay products.

THORIUM

Discovered in 1828 by the Swedish chemist J. J. Berzelius, thorium is named for Thor, the Scandinavian god of war. It is fairly widely distributed in nature, but is seldom found in concentrated deposits. The energy available from the world's thorium has been estimated to be more than that in all the uranium and fossil fuels, combined. The main commercial source for thorium is the mineral monazite, which contains from 3 to 9 percent thorium oxide, in addition to uranium, cerium, and other lanthanides.

Thorium extraction is a somewhat

complex process, since the element must first be separated from chemically similar elements. Several methods can be used to isolate the metal; it can be obtained by the reduction of its oxide with calcium; by electrolysis of anhydrous thorium chloride in a fused mixture of sodium and potassium chlorides; and by the reduction of its tetrachloride with an alkali metal. In its pure form, thorium is a silvery-gray metal with a melting point of about 1,700° C (about 3,092° F) and a boiling point in the neighborhood of 4,000° C (7,232° F). The oxide, ThO_2, has the highest melting point of all oxides–3,300° C (5,972° F). When traces of the oxide are present, thorium changes from lustrous gray to black in the air; as a powder, it ignites spontaneously. It is very slightly soluble in hydrochloric acid.

Since 1880 thorium has been used as a source of light in gas mantles. Presently, it finds application in the electronics industry and in catalytic processes. Perhaps its most promising use is in the nuclear industries, where it is used to produce the isotope uranium-233 by fission with low-speed neutrons:

$$^{232}Th + n \rightarrow {}^{233}Th + \gamma \rightarrow {}^{233}Pa + \beta \rightarrow {}^{233}U + \beta.$$

Thorium has a stable valence of +4 and, like actinium, it can form halide compounds. Its sulfate is a purple solid, and it forms many inorganic and organic complexes.

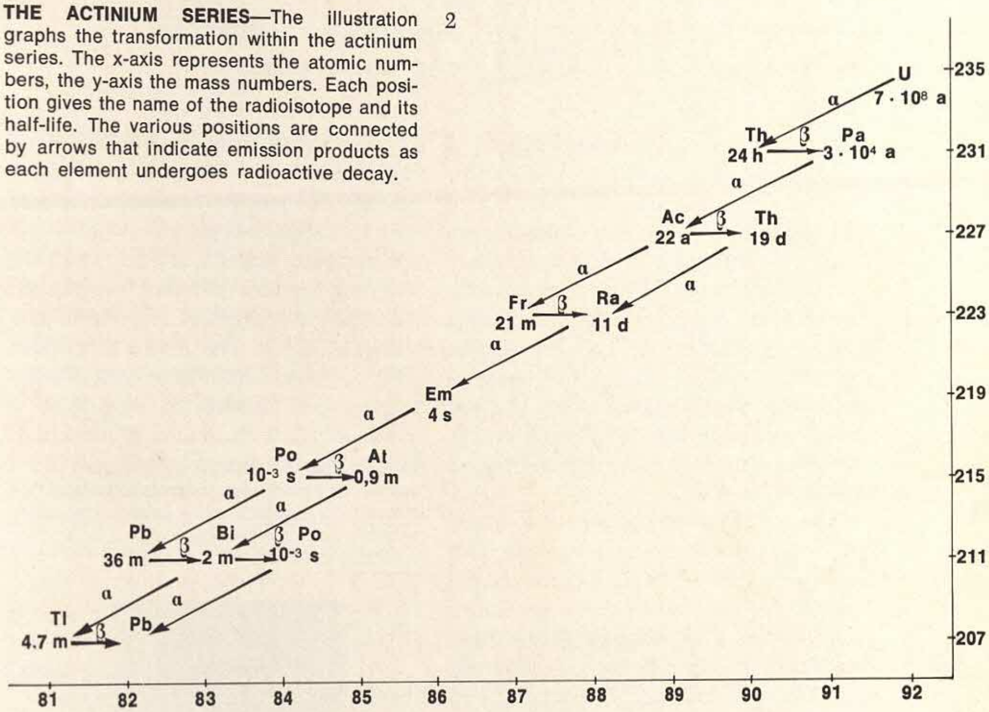
PROTACTINIUM

After its existence had been predicted by Mendeleev, who called it ekatantalum, protactinium was finally discovered in 1917 by several researchers working independently. Originally, it was called *proto*actinium because the isotope first discovered, protactinium-231, precedes actinium in the radioactive series (not to be confused with the periodic table). Although the oxide Pa_2O_5 had been prepared seven years previously, it was not until 1934 that pure metal was obtained.

Protactinium is the rarest of all the elements, either natural or man-made. Certain high-grade ores contain about three parts per million, but pitchblende yields only about one part protactinium-231 to 10 million parts ore. Obviously, isolation techniques present enormous problems. By a complex 12-stage British process, however, about 125 g (about 4.4 oz) of the element have been made available from 60 tons of uranium wastes. This presently represents the world supply, and the cost per gram is about $2,800. Gram quantities have been produced from thorium-230 in the reaction:

$$^{230}Th + n \rightarrow {}^{231}Th + \gamma \rightarrow {}^{231}Pa + \beta.$$

Metallic protactinium has an estimated melting point of 1,230° C (2,246° F); a boiling point has not been determined. Its structure is that of tetragonal crystals. In aqueous solutions the element's compounds hydrolyze easily into polymers, which makes the study of its properties difficult. Protactinium forms oxides and halides and many ion complexes.



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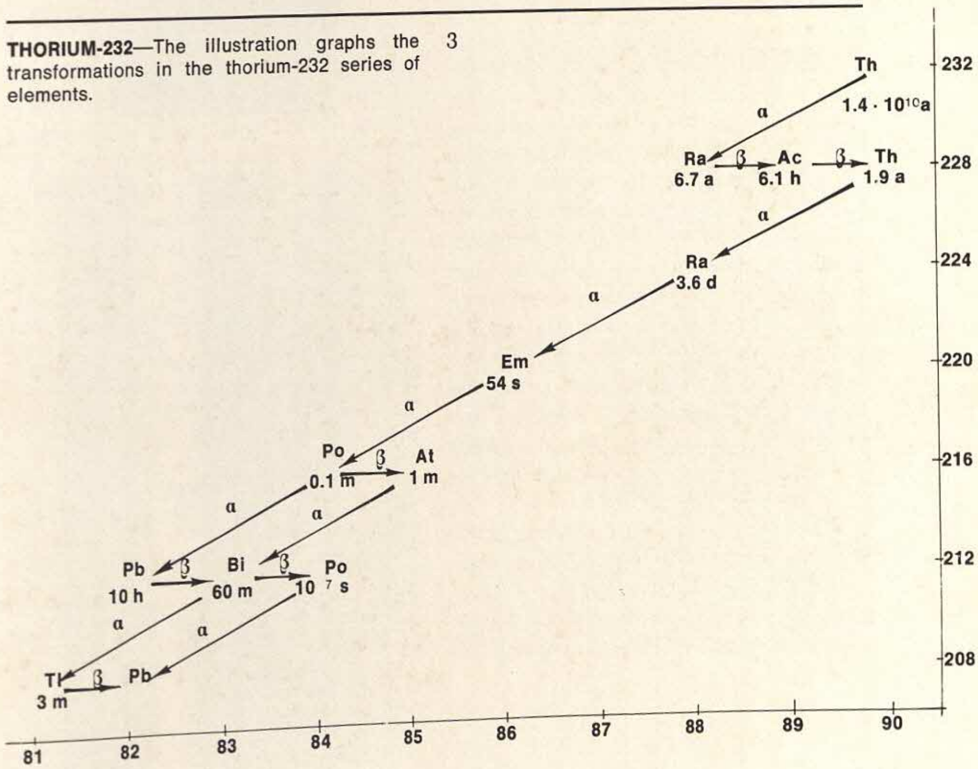
THE ACTINIUM SERIES—The illustration graphs the transformation within the actinium series. The x-axis represents the atomic numbers, the y-axis the mass numbers. Each position gives the name of the radioisotope and its half-life. The various positions are connected by arrows that indicate emission products as each element undergoes radioactive decay.



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THORIUM-232—The illustration graphs the transformations in the thorium-232 series of elements.

FROM GROUP IIIA TO GROUP 0 | semimetals, nonmetals, and noble gases

One of the distinguishing features of the elements is their electrochemical behavior. Those elements in Group IA of the periodic table, for example, are strongly electropositive with a definitely metallic character. At the other extreme, the elements of Group VIIA are strongly electronegative and exhibit nonmetallic properties. The noble gases of Group 0 show little or no tendency to act as either metals or nonmetals, and for all intents and purposes are neither electropositive nor electronegative.

There is yet another group of elements that possesses dual characteristics. This "non series" falls between the metals and nonmetals, and its members are drawn from Groups IIIA through VIIA. These are the semimetals, running in a diagonal line from boron (atomic number 5) to astatine (atomic number 85). The other elements in this family are silicon (14), arsenic (33), and tellurium (52). Depending upon the types of compounds formed, the compounds of these elements can exhibit either metallic or nonmetallic behavior. Both acids and bases are formed. For instance, metallic characteristics are seen when oxides are formed, which in the presence of water yield basic solutions. On the other hand, their nonmetallic anhydrides in water produce acids.

GROUP IIIA

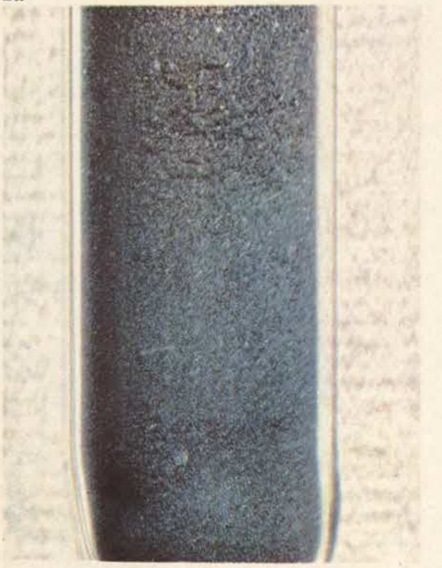
The elements in this group are boron (5), aluminum (13), gallium (31), indium (49), and thallium (81). Aluminum and boron are relatively abundant in nature; the others, though widely distributed, appear only in small quantities in their respective ores. With the exception of boron (one of the semimetals), all the elements in this group are markedly metallic. In fact, in any given group the metallic properties of its members become more pronounced with an increase in atomic radius, which is also an increase in atomic number.

All of the Group IIIA elements have three electrons in the outermost shell, producing trivalent cations. Boron, however, has a relatively small atom, so that its electrons are held somewhat tightly by the nucleus. This accounts for the fact that it forms B^{+3} compounds only with strongly electronegative elements. In general, its compounds are covalent.

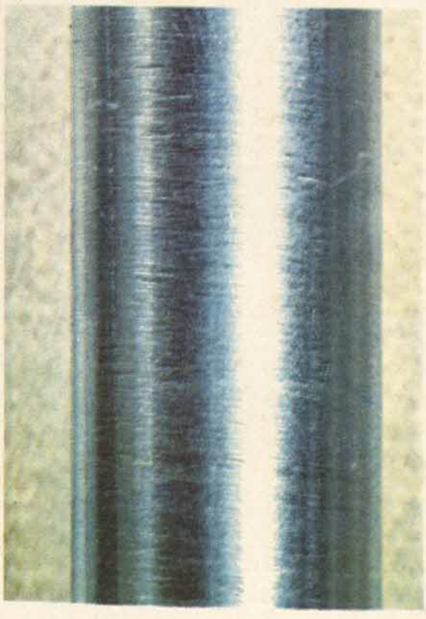
Aluminum, gallium, indium, and thallium all produce trivalent compounds. Additionally, thallium also forms univalent materials. The oxides of gallium, indium, and thallium have basic characteristics that increase in proportion to their atomic weights. One of boron's oxides is a weak acid anhydride; the other, with the same formula (B_2O_3), is a vitreous compound similar to glass. Aluminum oxide can behave both as an acid anhydride and a basic oxide. Its hydroxide, $Al(OH)_3$, is an electrolyte with amphoteric characteristics, which means that it can form acids or bases. It functions as an acid to yield hydrogen ions in solution or as a base, producing hy-

BORON AND ALUMINUM—Illustration 1a is a sample of boron, one of the semimetals. The metal in 1b is aluminum, a strong, lightweight element that is quite ductile and is a good electrical conductor.

1a



1b



2a

2b

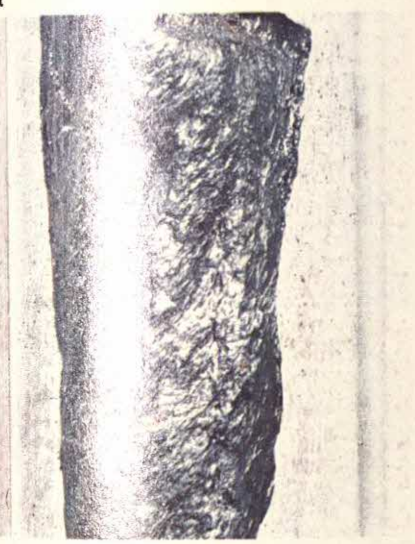
GALLIUM AND INDIUM—The elements in these illustrations are rather rare. Gallium (Illustration 2a) has the odd property of weighing less in the solid state than as a liquid, a characteristic of bismuth and ice. Indium is shown in Illustration 2b.

droxyl ions, depending on its environment.

GROUP IVA

Carbon (6), silicon (14), germanium (32), tin (50), and lead (82) are the family members of this group. Silicon is second in abundance only to oxygen in the Earth's crust. Carbon is a component of more than 90% of all known chemical compounds. Each of the IVA elements has four electrons in the valence shell. Because eight electrons in the outermost shell, for these elements, represents a full electron-complement, each should be readily able to either gain or lose four electrons. In fact, carbon and silicon tend to form covalent compounds, but tin and lead produce ionic bonds with other matter. Further, these differences in bonding account for considerable variance in melting points; carbon and silicon are nonmetallic and melt at high temperatures; tin and lead are metallic and melt at much lower temperatures.

3a



3b

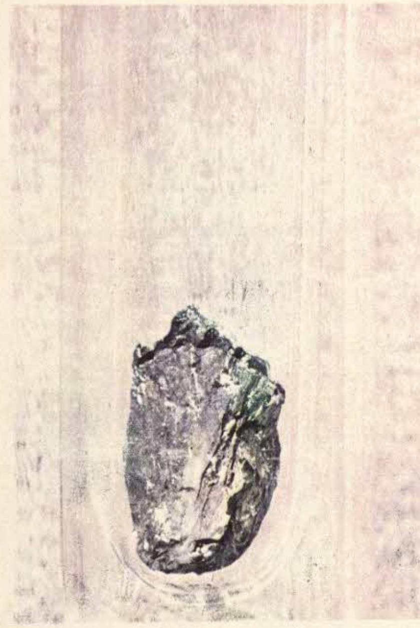
In addition to their valence of 4 (tetravalence), all these elements have a +2 state. In compounds of germanium, tin, and lead, it is the +2 oxidation state that forms the more stable compounds. The bivalent lead compounds are the most stable of this element, a demonstration that stability is directly related to increasing atomic weight.

The ability of the Group IVA elements to form compounds with hydrogen decreases with atomic weight. Hydrocarbons are numerous, well known, and necessary for life. Lead, however, produces only one compound with hydrogen—the hydride. In the formation of oxygen compounds, the elements form acidic substances when in the tetravalent state, with decreasing acidity as the atomic weight increases.

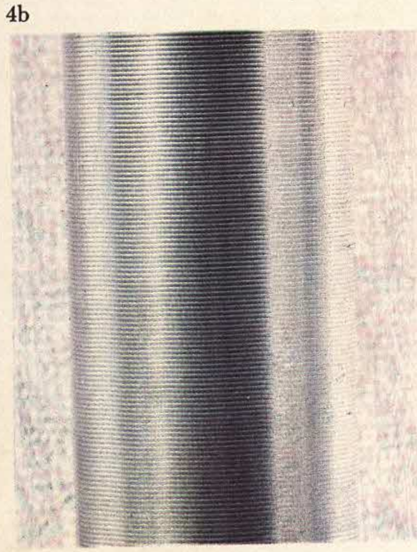
GROUP VA

The Group VA elements, all with five electrons in the outermost shell, are nitrogen (7), phosphorus (15), arsenic (33), antimony (51), and bismuth (83). This is a group of elements in which the

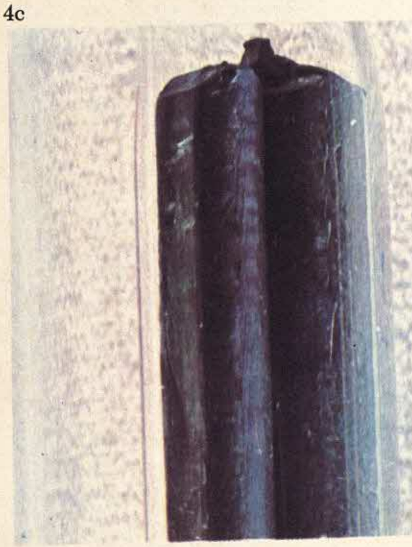
4a



4b



4c

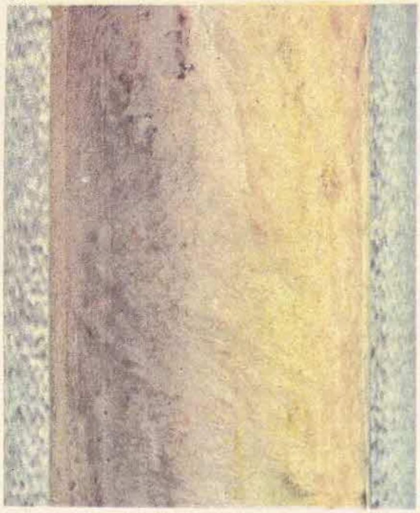


CARBON AND SILICON—Very similar to one another, carbon (Illustration 3a) and silicon (Illustration 3b) are tetravalent elements having both electronegative and electropositive properties. Present in all organic compounds, carbon can be replaced by silicon in some cases. Silicon is a vital component of many semiconductor devices.

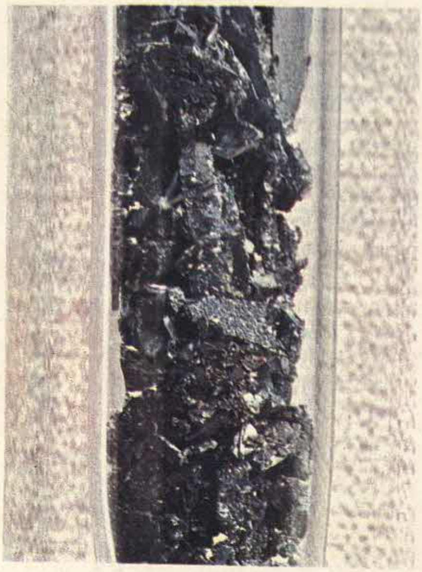
GERMANIUM, TIN, AND LEAD—The transistor industry owes its origins to germanium (Illustration 4a), a crystalline, brittle, metallic element. Tin (Illustration 4b) is the familiar plating material on tin cans, and is a silver-white metal with good malleability. The lead sample in Illustration 4c is representative of a metal known and used for centuries. Lead pipes in working condition have been found in ancient Roman ruins. Lead is the final radioactive decay-product of uranium.

PHOSPHORUS AND ARSENIC—Illustration 5a shows yellow phosphorus, an element essential to plant growth. Arsenic, shown in Illustration 5b, has applications beyond its well known use as a poison. It is used in the manufacture of transistors, and one of its compounds is used as a laser material.

5a

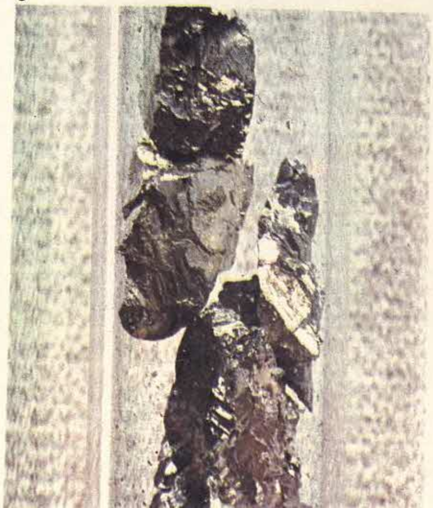


5b



ANTIMONY—Like lead, antimony has been known since ancient times in its compounds and perhaps in the metallic state. It is used today in products as widely varied as medicines and paints, alloys, and flameproofing compounds.

6



first member is a gas and the last a metal. (The IA group does not actually have hydrogen as its first member because this gas is generally considered separately.)

The VA elements gain or lose electrons with relative ease, combining with electronegative matter in the elements' +3 or +5 states and with electropositive elements in the −3 state (except bismuth). In the −3 oxidation state, the compounds formed by the VA elements contain a pair of free electrons, as in ammonia.

Nitrogen is the only element to have the wide-ranging valences from −3 to +5. It is the major gaseous constituent of the Earth's atmosphere, and is vitally important to the maintenance of the plant and animal life cycles. Nitrogen and phosphorus are typical nonmetals, while arsenic is one of the semimetals, and antimony and bismuth possess essentially metallic properties. The behavior of this group, like other groups, shows a gradual change from nonmetallic to metallic, with the increasing atomic radii, corresponding to increasing atomic numbers. This also accounts for the increasing alkalinity of their oxides. Finally, these elements are quite stable in the elementary state, and all have strong oxidizing properties in the pentavalent compounds.

GROUP VIA

This group is composed of oxygen (8), sulfur (16), selenium (34), tellurium (52), and polonium (84), all with six outer-shell electrons. Oxygen and sulfur are readily found in nature, with the former being the most abundant element in the Earth's crust. In small quantities, selenium is widely distributed; tellurium and polonium, on the other hand, are quite rare. Similar to the nitrogen family (VA), the elements of VIA are gaseous at the lowest atomic number and solid as the atomic number increases.

The maximum oxidation state of the VIA elements is +6, and all but oxygen also have +4 valences. In addition, all have −2 states; polonium has a +2 form. The higher oxides of these elements are all acid in character, and they all form compounds with hydrogen of the general formula nH_2. The most important of these compounds is water, without which

7a

7b

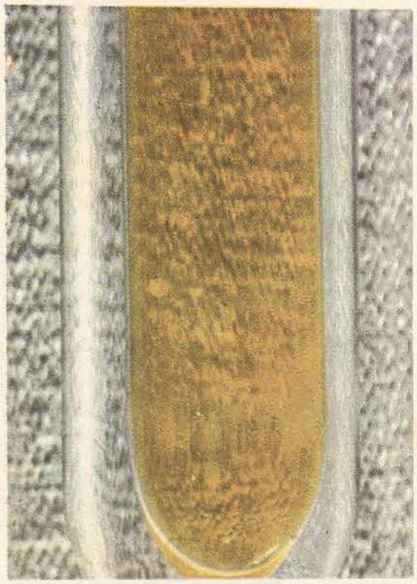
7c

BISMUTH, SULFUR, AND SELENIUM—Bismuth (Illustration 7a) is similar to antimony as a metal and in its compounds. Sulfur (Illustration 7b), the brimstone of the witch hunters, is a widely distributed element with innumerable uses. Selenium (Illustration 7c) is a somewhat rare element with the ability to change alternating current to direct current, and is thus used as a rectifier in electronic circuits.

8

TELLURIUM—Found in both the native and combined state in nature, this semimetal is brittle and in the pure state is silvery-white. It is used in ceramics.

9



CHLORINE—Under normal conditions, chlorine is a greenish-yellow gas with an irritating odor. Like all of the halogens, it is a powerful oxidizing agent.

10

BROMINE—This halogen, one of only two elements that are liquid at room temperature, is less reactive than fluorine or chlorine, but can, nevertheless, cause serious burns.

there could be no life on Earth. Lastly, there is a gradual but marked decrease in oxidizing power from oxygen to polonium, and the hydrogen compounds of selenium, tellurium, and polonium have greater reducing characteristics than hydrogen itself.

GROUP VIIA

This is the halogen group of elements that contains fluorine (9), chlorine (17), bromine (35), iodine (53), and astatine (85). Astatine is not found in nature; it is produced synthetically by nuclear reaction.

The physical properties of the halogens vary uniformly from one element to the next in the group, with specific gravities, melting and boiling points, and the influence of temperature on dissociation rising with the atomic weights. All have seven electrons in the outermost shell and show a strong tendency to acquire one electron to produce very stable negative ions. Hydrogen affinity decreases and oxygen affinity increases directly with atomic weight.

The halogens combine directly with metallic elements to form halides, and metals must be protected from the corrosive action of these elements. All are strong oxidizing agents and will cause severe damage to the skin and mucous membranes. Fluorine, in fact, is one of the most active of elements.

GROUP 0

The last of the groups in the periodic table contains the noble gases, so called because of their extreme inertness. The family members here are helium (2), neon (10), argon (18), krypton (36), xenon (54), and radon (86). All but radon are found in the atmosphere in minute quantities. Radon is a product of the radioactive decay of radium.

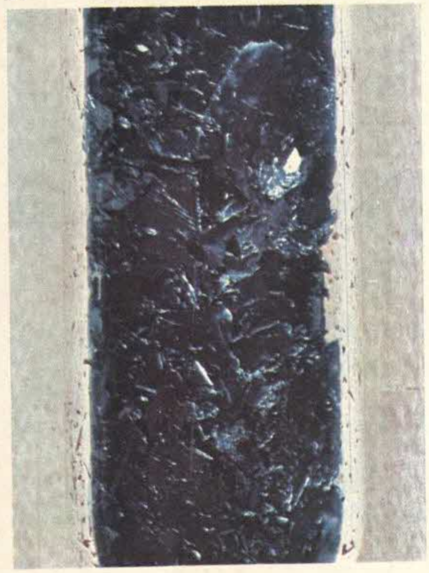
The outermost shells of the Group 0 elements are completely filled—they have no tendency to join with other elements. Thus, naturally occurring noble-gas compounds are unknown, although sophisticated techniques have been devised to prepare noble gas compounds with very reactive elements such as fluorine.

The noble gases are good electrical conductors at high voltages. "Neon" signs contain one or more of these gases that are ionized by high voltages—the degree of ionization is high enough to cause the glow. The color of the sign is dictated by the kind of gas in the tubes. In the commercial preparation of noble gases, helium is sometimes extracted from natural gas, while the others are usually obtained by the fractional distillation of air.

An element's characteristics depend on the element's position in the periodic table. Many of an element's properties can be forecast simply by knowing its location in the table. After Mendeleev's initial table became known, for example, researchers not only postulated the existence of many elements then unknown but were even able to predict correctly some of the elements' characteristics. Two major components of the table were omitted by Mendeleev: the existence of the noble gases and the properties of the radioactive elements.

IODINE—Perhaps the best known of the halogens, iodine is solid, forming beautiful purple-black crystals. When heated it gives off an irritating vapor. In contrast to the gaseous halogens, iodine tends to form monoatomic molecules.

11



THE TRANSITION ELEMENTS FROM IRON TO MERCURY | tools, medicine, paint, and money

In the approximate center of the periodic table, comprising Group VIII, are the transition elements, all metals, from iron (atomic number 26) to platinum (atomic number 78). Group VIII is made up of three triads of elements, with the members of each triad closely resembling one another both chemically and physically.

The first series, the iron triad, is composed of iron (26), cobalt (27), and nickel (28). Next is the palladium triad, of ruthenium (44), rhodium (45), and palladium (46). Finally, there is the platinum triad, whose members are osmium (76), iridium (77), and platinum (78). All these metals are grayish to silvery-white, have moderate to high melting points, and have almost constant atomic radii within the triad.

1

IRON—Known and used for centuries, this element has marked metallic properties. It forms more than 100 compounds in its +2 or +3 valence state. Ordinary rust is one form of iron oxide.

2

COBALT—A silver-white or gray metal, cobalt melts at 1,495° C (about 2,725° F). Its valences are +2 and +3. This metal imparts an intense blue color to glass, and its ^{60}Co isotope is the heart of the cobalt "bomb" used in medicine.

IRON TRIAD

Iron, nickel, and cobalt are clearly metallic in character. Their melting points are moderately high, ranging from 1,453° to 1,535° C (about 2,645° to 2,795° F).

In their stable forms, all of these elements are ferromagnetic at ordinary temperatures. This means that under the influence of a magnetic field they become magnetic, and remain so after removal of the field. This property is due to unpaired electrons in the incomplete electron levels. At high temperatures, the metals are paramagnetic (weakly magnetic).

Iron, cobalt, and nickel each have valence states of 2 and 3. In the higher state they exhibit strong oxidizing properties. Because they also have incomplete inner electron levels, they easily form stable complexes, in which conditions the electron configuration approximates that of the noble gases.

PALLADIUM AND PLATINUM TRIADS

These triads can be examined in combination because the chemical and physical properties of their elements are similar. Because of their relative inertness, all six elements are found in nature in their elementary forms. All are poor reducing agents and oxidize only with difficulty.

Because of their similarity to one another, the ores of ruthenium, rhodium, palladium, osmium, iridium, and platinum are usually found together; the metals are sometimes found naturally alloyed. Separation of the elements is difficult because the presence of one element influences the chemical behavior of the others. Platinum, for example, is dissolved by aqua regia (a mixture of nitric and hydrochloric acids), while pure iridium is totally unaffected. If the two metals are in a mixture, however, the acid dissolves part of the iridium along

3

NICKEL—A durable, silvery-gray metal, nickel forms compounds in the +2 and +3 oxidation states. As a plating material it imparts a finish similar in appearance to silver. The five-cent U.S. "nickel" is 25 percent nickel, 75 percent copper. The illustration shows the metal in the powdered and spherical forms.

with the platinum.

The metals in these triads have oxidation states from 3 to 8, though iridium and rhodium have a strong tendency to form complexes with ammonia in their trivalent form. Palladium and platinum form quite stable complexes in the +2 and +4 states.

Because they adsorb hydrogen readily, these metals are used as catalysts. (In adsorption a liquid or a gas is held fast to a solid.) The physical state of the metal is important with respect to its hydrogen-adsorption properties. Palladium in sheet form, for example, adsorbs a volume of hydrogen hundreds of times its own volume. Finely divided platinum in suspension can adsorb a volume of hydrogen 1,200 times its own volume, and in a colloidal solution will adsorb up to 3,000 times its volume of the gas. The use of these elements is not restricted to hydrogen adsorption, however; platinum is used to a great extent in the catalytic oxidation of sulfur dioxide and ammonia and in the oxidation of carbon monoxide to carbon dioxide with water. In an alloyed form, rhodium is also used in the catalytic oxidation of ammonia.

The final six elements of the transition metals are found in the copper and zinc subgroups, IB and IIB, respectively. Some authorities exclude these subgroups from the transition elements, while others consider that the general properties of the elements place them in the terminal group of transition elements.

COPPER SUBGROUP

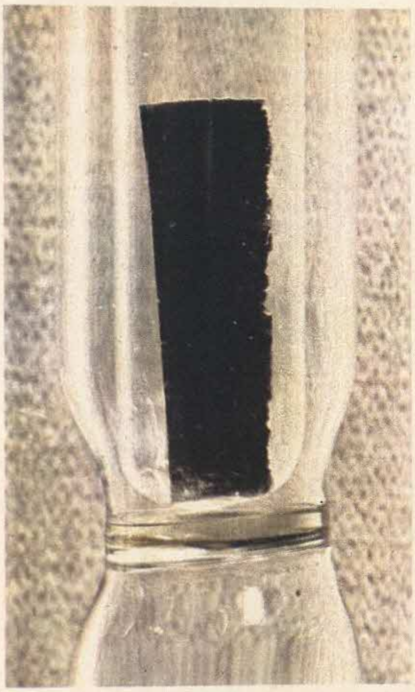
This group includes copper (29), silver (47), and gold (79), all clearly metallic in character. They are all ductile and excellent conductors of electricity and heat.

4

RUTHENIUM—A hard, brittle, grayish-white or silver metal, ruthenium takes its name from the Latin word for Russia, where it was discovered. It has valence states of 3, 4, 6, and 8. Ruthenium is widely used as a catalyst, and when used in alloys, it imparts mechanical strength to other metals.

RHODIUM—This metal has valences of 2, 3, 4, and 5, and in the pure state is silvery-white. At red heat it converts to an oxide, but at higher temperatures reverts to the metallic form. In plating, rhodium provides an exceedingly durable surface; the metal is used in jewelry making.

5

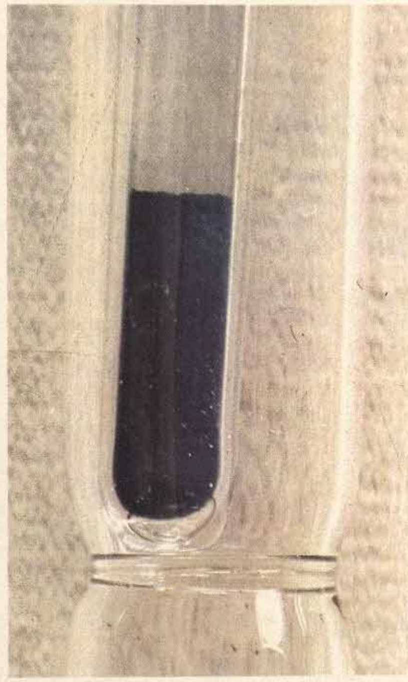


PALLADIUM—At room temperature, palladium can adsorb up to 900 times its own volume of hydrogen, a property used to purify the gas. White gold, as used in jewelry, is an alloy of gold decolorized by the addition of palladium.

6

OSMIUM—This metal takes its name from the Greek *osme,* meaning odor. While the solid metal is not affected by air at room temperature, in the powdered or spongy state it forms an oxide with a strong smell. The tetroxide is highly toxic, causing lung congestion, and skin or eye damage in concentrations as low as 10^{-7} grams/cubic meter. Almost all the osmium produced is used to make very hard alloys.

7



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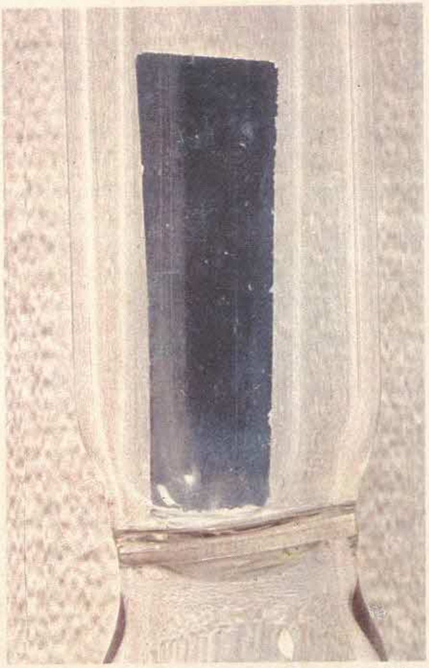
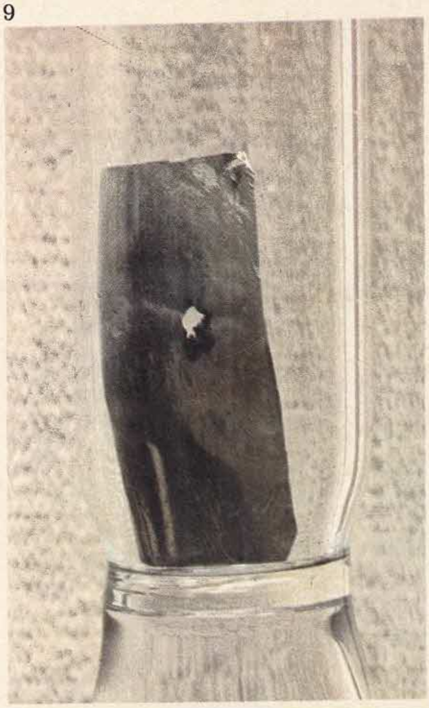


IRIDIUM—With a valence of 3 or 4, iridium forms very colorful salts. It is the most corrosion-resistant metal known. It is used mainly in alloys to harden platinum.

9



PLATINUM—This long-known and highly prized metal is impervious to ordinary chemical reagents, although it is dissolved by aqua regia to form the important compound chloroplatinic acid. Platinum has been used in a number of applications where resistance to high temperatures is required.

In fact, silver is the most efficient electrical conductor known (other than the recently discovered superconducting alloys), and research is constantly seeking economical use of this property. Silver is the most malleable and ductile of all metals except gold, and it can be beaten into leaves of less than 0.00025 mm thickness. The three metals have moderately high melting points, around 1,000° C (about 1,830° F).

Each metal in this subgroup has a single electron in the outermost shell, thus having the valence characteristics of the alkali-metal elements (Group IA). The next-to-outermost shell is complete, though it readily loses one or two electrons in the cases of copper and gold, respectively. Thus, silver has only one oxidation state, +1; copper has two, +1 and +2; and gold has two, +1 and +3. Although they have only one electron in the outermost shell, the elements differ considerably from the Group IA metals in certain chemical and physical properties. The copper subgroup elements are much more stable, they do not oxidize readily under normal conditions, and they readily form complexes with CN^- groups, ammonia, Cl^-, and other ions.

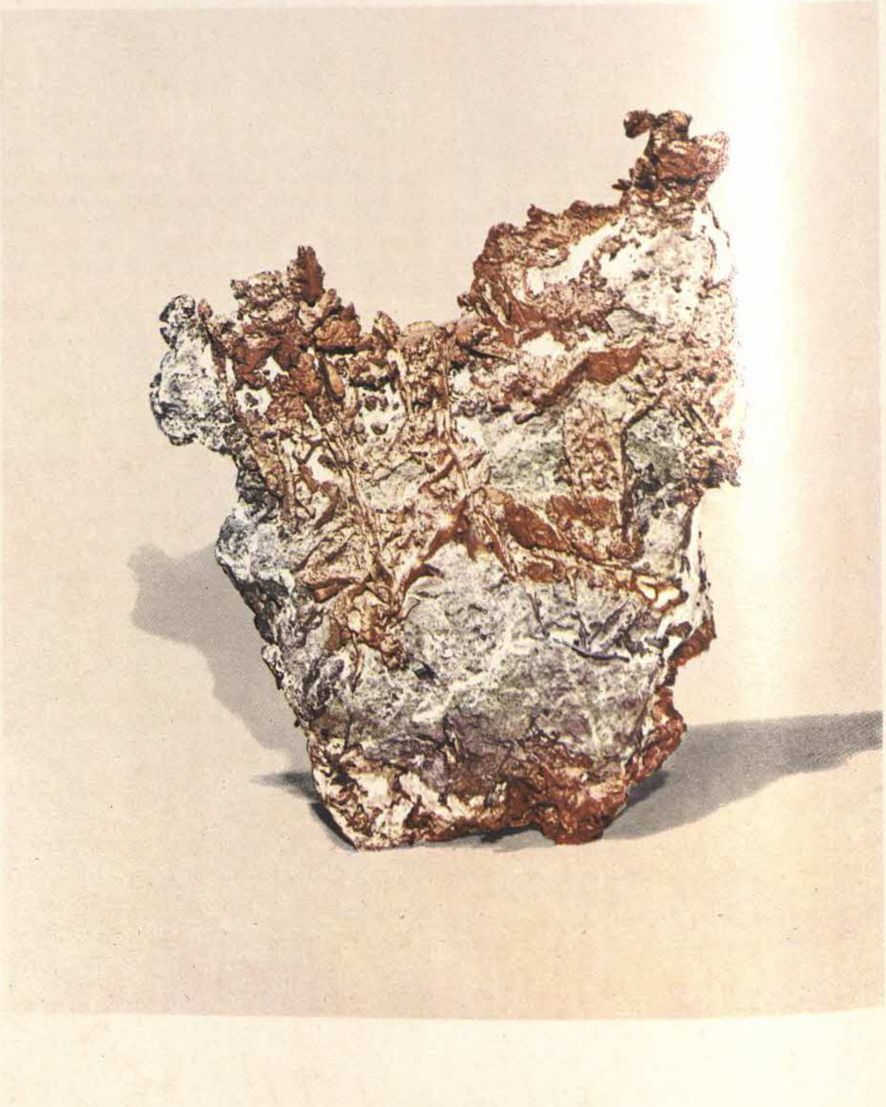
In the metallic state, copper, silver, and gold are fairly resistant to corrosion and atmospheric agents; this is particularly true of gold. Copper is generally alloyed with gold and silver to improve the mechanical properties of these precious metals.

ZINC SUBGROUP

The last of the transition metals are zinc (30), cadmium (48), and mercury (80). Mercury is unique in that it is the only

NATIVE COPPER—A reddish, ductile metal, metallic copper is found in the native state, and forms more than 100 compounds. It is widely used in metallurgy, where it adds strength and hardness to other metals (Illustration 10).

10



11

GOLD—Shown here in the granular state, gold is perhaps the most prized metal in the world. National economies are based on its stable value. Almost without exception, it is found in the native state. Besides its centuries-old use as jewelry, gold is now used as a radioactive tracer in medicine. It is the most ductile of all metals; one ounce of gold can be beaten into a sheet 300 feet square. Extremely inert, it is considered to be almost indestructible.

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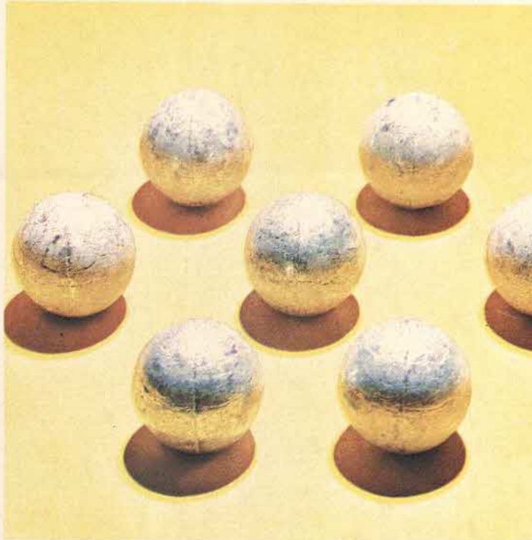


CADMIUM—This element is similar to zinc in many ways, and is most often found in association with zinc ores. It forms bivalent compounds, and is a component of some of the lowest melting-point alloys. Both the bluish-white metal and its compounds are highly toxic. Exposed workers usually incur warning symptoms before the lungs are damaged.

metal that is liquid at room temperature, and shares this property with only one other element—bromine.

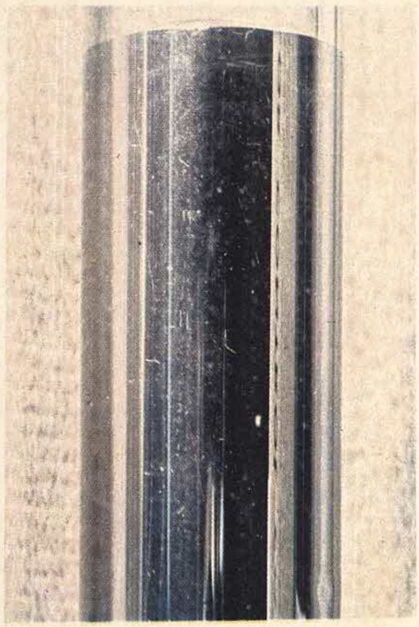
All three metals are bivalent, and mercury is also univalent. There is a similarity in electron configuration between the zinc subgroup and the alkaline-earth metals (Group IIA), each member of both families having two electrons in the outermost shell. In zinc, cadmium, and mercury, the next-to-outermost shell has a full electron complement.

Zinc's main ores are sphalerite, smithsonite, willemite, and franklinite. The metal is widely used to protect ferrous metals from oxidation. Cadmium is generally found in combination with zinc in its ores, and is finding increased use in dry cell batteries. Cadmium compounds also provide the basis for certain paint pigments. Mercury can be found in both the metallic state and combined with sulfur (cinnabar). Usually, however, mercury is mined as cinnabar. A unique element, mercury is used frequently in laboratory and clinical thermometers; in dental work it is used to form an amalgam with silver for fillings. Mercury is used as a fungicide, and in batteries and other electrical equipment.

12

ZINC—This bluish-white, lustrous metal is brittle at ordinary temperatures, but quite malleable between 100° and 150° C (212° and 302° F). It has a valence of +2, and forms many compounds in nature. With other metals, it forms numerous alloys, from type metal to spring brass. The common garbage can is protected from rust by a coating of zinc.

14



MERCURY—The only metal that is liquid at room temperature, mercury is sometimes called quicksilver. Its two oxidation states form a variety of compounds, from medicines to paint pigments. Mercury, its vapor, and some of its compounds are virulently poisonous—a fact not commonly appreciated. The most common mercuric ore is cinnabar.

ABBREVIATIONS

A	ampere
Å	Ångstrom unit
abs	absolute
a-c	alternating current (as an adjective)
amu	atomic mass unit
atm	atmosphere
at. wt	atomic weight
AU	astronomical unit
avdp	avoirdupois
Bev	one billion electron volts
bhp	brake horsepower
bhp-hr	brake horsepower-hour
bp	boiling point
Btu	British thermal unit
C	temperature Celsius; temperature Centigrade
c	candle
cal	calorie
cfm	cubic feet per minute
cfs	cubic feet per second
cgs	centimeter-gram-second (system)
cl	centiliter
cm	centimeter
cm^2	square centimeter
cm^3	cubic centimeter
coef	coefficient
colog	cologarithm
cos	cosine
cot	cotangent
cp	candlepower
csc	cosecant
cu	cubic
cu ft	cubic foot
db	decibel
d-c	direct current (as an adjective)
doz	dozen
E	electromotive force
e	the base of the system of natural logarithms
ev	electron volt
F	temperature Fahrenheit
fp	freezing point
fpm	feet per minute
fps	feet per second
ft	foot; feet
ft^2	square foot
ft^3	cubic foot
ft-c	footcandle
ft-lb	foot-pound
G	universal gravitational constant
g	gram
gal	gallon
g-cal	gram-calorie
gpm	gallons per minute
gps	gallons per second
hr	hour
$h\nu$	photon energy
hp	horsepower
Hz	hertz (cycles per second)
I	electric current
ID	inside diameter
in.	inch
$in.^2$	square inch
$in.^3$	cubic inch
in.-lb	inch-pound
ips	inches per second
j	joule
K	temperature Kelvin (absolute)
kcal	kilocalorie
kg	kilogram
kg-cal	kilogram-calorie
kg-m	kilogram-meter
kg/m^3	kilograms per cubic meter
kgps	kilograms per second
km	kilometer
kv	kilovolt
kw	kilowatt
kwhr	kilowatt-hour
l	liter; lumen
lat	latitude
lb	pound
lb-ft	pound-foot
lb/ft^2	pounds per square foot
lb/ft^3	pounds per cubic foot
lb-in.	pound-inch
l-hr	lumen-hour
lin ft	linear foot
log	logarithm (common)
$\log_e$	logarithm (natural)
long.	longitude
m	meter; minute (time, in astronomical circles)
m^2	square meter
m^3	cubic meter
ma	milliampere
Mev	one million electron volts
mg	milligram
mh	millihenry
mi	mile
mi^2	square mile
min	minute
m-kg	meter-kilogram
ml	milliliter
mm	millimeter
mm^2	square millimeter
mm^3	cubic millimeter
$m\mu$	millimicron
mph	miles per hour
mphps	miles per hour per second
mv	millivolt
N	Avogadro's constant
$n!$	factorial n
OD	outside diameter
oz	ounce
pH	rating on acid-alkaline scale
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
R	temperature Reaumur; resistance
RA	right ascension
rpm	revolutions per minute
rps	revolutions per second
sec	secant; second
sin	sine
sp gr	specific gravity
sq	square
tan	tangent
V	volt
VA	volt-ampere
W	watt; work
yd	yard
yd^2	square yard
yd^3	cubic yard

SCIENTIFIC SYMBOLS AND ABBREVIATIONS

α	alpha particle
β; β^-	beta particle
β^+	positron
γ	gamma radiation
Δ	a small change; heat
λ	wavelength; radioactive-decay constant
ma	milliampere
μc	microcurie
μf	microfarad
$\mu in.$	microinch
μm	micron
$\mu\mu$	micromicron
$\mu\mu f$	micromicrofarad
ν	frequency; neutrino
π	3.14159; osmotic pressure
Σ	the sum of
σ	nuclear cross section (barns); area
Ω	electrical resistance (ohms)
ω	angular speed; angular velocity
$'$	minute (angular measure)
$''$	second (angular measure)
♂	male
♀	female
$>$	is greater than
$<$	is less than
$\propto$	is proportional to
∞	infinity
$\sqrt{\ }$	square root of
$^\circ$	degrees; temperature; angle measurement (example, 30°)
[ ]	molar concentration
$+$	positive electric charge; mixed with; plus
$-$	negative electric charge; single covalent bond; minus
$=$	equals; double covalent bond; produces
$\neq$	does not equal
$\equiv$	triple covalent bond
$\rightarrow$	produces; forms; chemical reaction
$\rightleftarrows$	reversible chemical reaction
$\uparrow$	gas produced by a chemical reaction
$\downarrow$	precipitate produced by a chemical reaction
*	radioactive substance (follows symbol of element; example, Cl^*)

THE ILLUSTRATED SCIENCE DICTIONARY

Haber Process to Induction

KEY TO PRONUNCIATION

The diacritical marks are:

ə	b*a*nan*a*, *a*but	e	b*e*t	th	*th*in
ᵊ	preceding l, m, n as in batt*le*	ē	b*ea*t	t̲h̲	*th*en
ə̇	*e*lectric	i	t*i*p	ü	r*u*le, f*oo*l
ər	f*ur*ther	ī	b*i*te	u̇	p*u*ll, w*oo*d
a	m*a*t	j	*j*ob, gem	ue	German h*ü*bsch
ā	d*ay*	ŋ	si*ng*	u̅e̅	French r*ue*
ä	cot, f*a*ther	ō	b*o*ne	yü	*u*nion
au̇	n*ow*, *ou*t	ȯ	*saw*, *a*ll	zh	vi*si*on
		ȯi	c*oi*n		

ˈ mark preceding the syllable with strongest stress.

ˌ mark preceding a syllable with secondary stress.

H

Haber process \\'hä-bər 'präs-ˌes\\

CHEMISTRY. A chemical process that combines hydrogen and nitrogen, under pressure, at a high temperature and in the presence of a catalytic agent, to form ammonia, NH_3.

The ammonia yielded by the HABER PROCESS *has many important uses, among which is the production of nitric acid and fertilizer.*

habit \\'hab-ət\\ *n.*

1. ZOOLOGY. A characteristic, acquired by repetition, of acting in a certain manner. 2. EARTH SCIENCE. The characteristic shape or combination of forms of crystal growth; also, the general shape of a mineral that is controlled by the shape and relative proportions of its crystal faces.

The feeding HABIT *of a bird or other animal may be changed by a new environment.*

habitat \\'hab-ə-ˌtat\\ *n.*

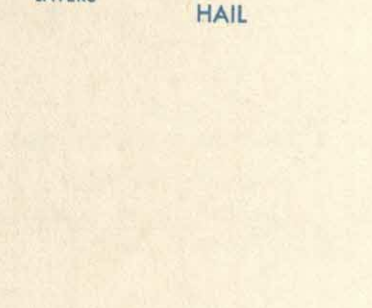
BIOLOGY. The natural living place of an animal or plant.

Cold, fresh, clear water is the HABITAT *of the rainbow trout.*

hail \\'hāl\\ *n.*

EARTH SCIENCE. Pellets of ice that form as frozen raindrops in cumulonimbus clouds. Viewed in cross section, these pellets frequently have a layered or onionlike structure.

HAIL *increases in size as the individual pellets pass through zones of supercooled water vapor where additional water freezes onto them.*



half-life \\'haf-ˌlīf\\ *n.*

PHYSICS. The length of time required for half of the atoms of a given amount of a radioactive element to disintegrate. It is the unit used in measuring the rate of disintegration of radioactive substances.

The HALF-LIFE *of uranium 238 is* 4.5×10^9 *years.*

half-reaction \\'haf-rē-'ak-shən\\ *n.*

CHEMISTRY and PHYSICS. Either of the changes that take place within an electric cell. One half-reaction is the dissolving of the negative electrode to form ions. The other half-reaction is the depositing of electrons on the positive electrode.

In an electric cell, each kind of HALF-REACTION *is necessary to produce electricity.*

HALLEY'S COMET

halide \ˈhal-ˌīd\ *n.*

CHEMISTRY. Any compound composed of one of the halogens (chlorine, bromine, fluorine, iodine and astatine) and another element, generally a metal. One example is sodium chloride, NaCl, commonly known as table salt.

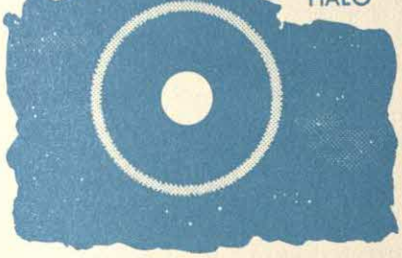
Because the HALIDE *silver bromide, AgBr, is sensitive to light, it is used in making photographic film.*

Halley's comet \ˈha-ˌlēz ˈkäm-ət\

ASTRONOMY. A comet named in honor of the astronomer Edmund Halley, who predicted its return. It appears at intervals averaging 77 years and is the only great comet that returns at intervals of less than several hundred years.

The records of the appearance of HALLEY'S COMET *date back to 240 B.C., and its next appearance is predicted for 1986.*

HALO



halo \ˈhā-(ˌ)lō\ *n.*

EARTH SCIENCE. A colored ring of light that encircles the sun or moon; also, a circle of light around the sun or moon when viewed through a cirrostratus cloud. A halo is caused by refraction of light in ice crystals or water vapor in the upper atmosphere.

A HALO *is sometimes colored like a rainbow.*

halogen \ˈhal-ə-jən\ *n.*

CHEMISTRY. One of a family of nonmetallic elements (chlorine, bromine, iodine, fluorine or astatine) that has seven electrons in its outermost shell.

The word HALOGEN *comes from Greek words meaning "salt former."*

halogenation \ˌhal-ə-jə-ˈnā-shən\ *n.*

CHEMISTRY. The reaction of a halogen with an organic compound, such as the reaction of chlorine, Cl_2, with methane, CH_4.

The complete HALOGENATION *of methane with chlorine produces the common solvent carbon tetrachloride,* CCl_4.

HALOPHYTES

halophytes \ˈhal-ə-ˌfīts\ *n.*

BOTANY. Plants that grow either in alkaline or salty soil.

The HALOPHYTES *are one of four plant groups that are classified on the basis of their water requirements.*

hanging valley \'haŋ-iŋ 'val-ē\

EARTH SCIENCE. A valley of a tributary stream whose floor is higher than the level of the main stream or shore.

The stream flowing in a HANGING VALLEY *usually empties by waterfall into a larger stream, lake or ocean.*

HANGING VALLEY

haploid \'hap-ˌlȯid\ *adj.*

BIOLOGY. Pertaining to a cell that has only half the number of chromosomes present in a zygote or somatic cell; equivalent to monoploid.

All cells of the gametophyte generation in plants such as ferns and mosses have the HAPLOID *number of chromosomes.*

haploid number \'hap-ˌlȯid 'nəm-bər\

BIOLOGY. The number of chromosomes characteristic of reproductive cells; the n number of chromosomes.

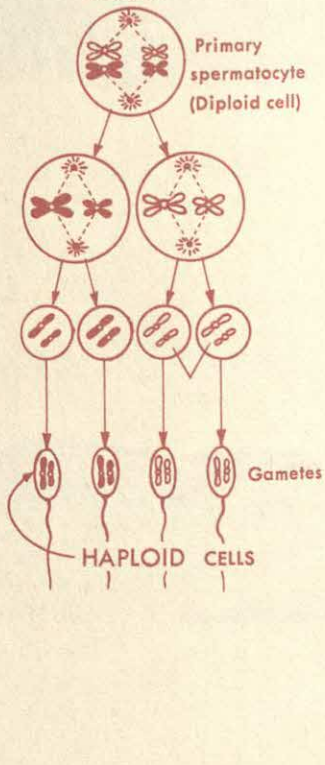
Reproductive cells, known as gametes, have a HAPLOID NUMBER, *or n number, of chromosomes, but fertilized eggs and body cells have a diploid, or 2n, number.*

hardness \'härd-nis\ *n.*

1. EARTH SCIENCE. The resistance of a solid material to surface abrasion or cutting, as determined by its ability to scratch or withstand scratching by another solid; see *Mohs' scale*. 2. PHYSICS. The quality of X rays that determines how much they will penetrate a given substance. 3. ENGINEERING. The resistance of a solid material to deformation or penetration. 4. CHEMISTRY. See *hard water, temporary hardness* and *permanent hardness.*

The HARDNESS *of a mineral is one of the properties used in identifying it.*

MEIOSIS



hardpan \'härd-ˌpan\ *n.*

EARTH SCIENCE. The firmly-packed layer of earth, usually clay particles cemented by insoluble materials, that lies beneath the soil.

HARDPAN *limits the downward movement of water and the downward growth of plants.*

hard water \'härd 'wȯt-ər\

CHEMISTRY. Water containing certain dissolved salts that produce generally-undesirable effects, such as forming insoluble compounds with soap and clogging hot-water pipes with precipitates.

Some detergents contain a substance, such as borax, to soften HARD WATER.

Hardy-Weinberg principle \ˈhärd-ē ˈwīn-bərg ˈprin(t)-s(ə-)-pəl\

BIOLOGY. An equation stating that, under random mating conditions, a large animal or plant population produces a constant variety of genotypes as long as other conditions remain constant.

The HARDY-WEINBERG PRINCIPLE *is basic to the study of population genetics.*

harmonic frequencies \här-ˈmän-ik ˈfrē-kwən-sēz\

PHYSICS. A series of frequencies resulting from the fundamental frequency of a vibration, each harmonic frequency having two, three or more times the number of vibrations or waves as the fundamental frequency. It is expressed as cycles per second. In music, the harmonic frequencies produce overtones.

Without HARMONIC FREQUENCIES, *the tone of a musical instrument is colorless.*

harmonic motion \här-ˈmän-ik ˈmō-shən\

PHYSICS. A type of periodic motion produced by an elastic body. Simple harmonic motion has one frequency and amplitude. It extends to points equidistant from equilibrium position. Acceleration of motion is in direct proportion to the distance from equilibrium position.

The motion of a spring or of a clock pendulum is typical of HARMONIC MOTION.

harmonic progression \här-ˈmän-ik prə-ˈgresh-ən\

MATHEMATICS. A sequence of terms whose reciprocals, taken in order, form an arithmetic progression.

The sequence $\frac{1}{1}, \frac{1}{3}, \frac{1}{5}, \frac{1}{7}, \frac{1}{9}, \frac{1}{11}$ *is a* HARMONIC PROGRESSION.

Haversian canal \hə-ˈvər-zhən kə-ˈnal\

ANATOMY. One of the tiny canals forming a network through which blood vessels pass into and through bones.

The blood vessels within a HAVERSIAN CANAL *carry nourishment to living bone cells.*

headland \ˈhed-lənd\ *n.*

EARTH SCIENCE. A high point or projection of land into a lake or a sea; also, the source area of a stream.

A HEADLAND *is sometimes referred to as a cape, a head, a promontory or a tongue.*

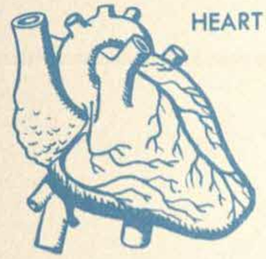
headwaters \ˈhed-ˌwȯt-ərz\ *n.*

EARTH SCIENCE. The small streams that form the beginning, or source, of a river.

The HEADWATERS *of the Missouri River are located on the eastern slope of the Rocky Mountains.*

heart \'härt\ *n.*
ANATOMY and ZOOLOGY. Any hollow, muscular organ of an animal that maintains circulation of the blood by alternate dilation and contraction.

In mammals and birds, the HEART *has four chambers.*

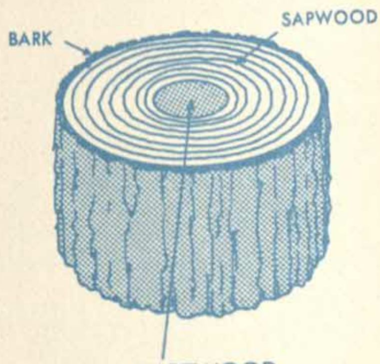


heartwood \'härt-ˌwu̇d\ *n.*
BOTANY. Wood occupying the inner cylinder of a tree stem. It is usually darker than the outer wood and is made up of dead tissue, often filled with gums and resins.

The HEARTWOOD *of a tree is also called the duramen.*

heat \'hēt\ *n.*
PHYSICS. A form of energy that melts, evaporates or raises the temperature of a substance; also, the internal energy of a substance, associated with the kinetic energy of its molecules and atoms.

HEAT *is measured by either the calorie or the British thermal unit.*



heat barrier \'hēt 'bar-ē-ər\
AERONAUTICS and ASTRONAUTICS. A limitation imposed on the speed of aircraft due to the intense heating created by the friction of air passing over the surface of the vehicle.

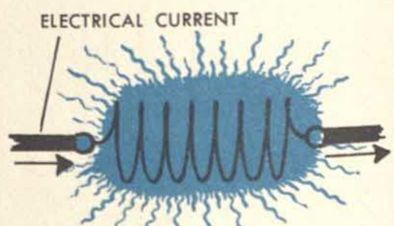
Because of the HEAT BARRIER, *special alloys and ceramic materials have been developed for high-speed aircraft and space vehicles.*

heat engine \'hēt 'en-jən\
ENGINEERING. Any one of several types of engines, as steam, diesel, gasoline, steam-turbine or jet-propulsion, operating on the principle that heat gives increased motion to molecules and releases energy in the form of expanded gases.

The early engine driven by steam was a much less efficient HEAT ENGINE *than the modern diesel engine.*

heat exhaustion \'hēt ig-'zȯs-chən\
MEDICINE and PHYSIOLOGY. A condition caused by overexposure to high temperatures, usually accompanied by symptoms such as abdominal cramps, dizziness, rapid pulse and low blood pressure.

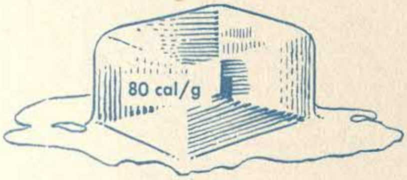
Sunstroke is a dangerous form of HEAT EXHAUSTION.



heating element \'hēt-iŋ 'el-ə-mənt\
ENGINEERING. That part of an electrical heating system or device

that transforms electrical energy into heat energy; also, generally, an alloy having a high resistance, used to make a filament.

A coiled wire made of a nickel-chrome alloy is generally used as the HEATING ELEMENT *of a toaster.*



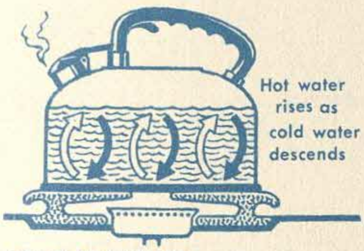
HEAT OF FUSION (OF ICE)

heat of formation \'hēt əv fȯr-'mā-shən\
CHEMISTRY. The amount of heat that is absorbed or released when one mole of a compound is formed from its component elements.

Since most compounds have a positive HEAT OF FORMATION, *energy is given off when they are formed.*

heat of fusion \'hēt əv 'fyü-zhən\
PHYSICS. The amount of heat required to melt one unit of mass of a given solid at its melting point, thus changing it to a liquid at the same temperature.

The HEAT OF FUSION *of a solid is commonly expressed as a given number of calories per gram of that solid.*



HEAT TRANSFER (CONVECTION)

heat of vaporization \'hēt əv ˌvā-p(ə-)rə-'zā-shən\
CHEMISTRY. The amount of heat required to convert a unit mass of liquid at its boiling temperature into a vapor at the same temperature.

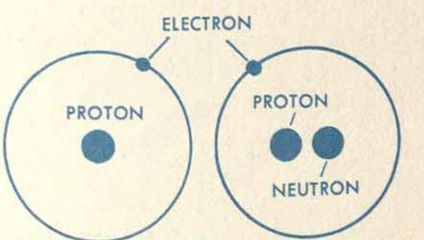
The HEAT OF VAPORIZATION *of water is about 540 calories per gram at 100° C.*

heat sink \'hēt 'siŋk\
PHYSICS. A device that absorbs heat or that dissipates it away from components that it might otherwise damage.

One type of HEAT SINK *transfers heat away from electronic equipment that operates at high temperatures.*

heat transfer \'hēt 'tran(t)s-ˌfər\
PHYSICS. Any of three methods of moving heat energy from one place to another: conduction (as through solids or stationary liquids), convection (as by moving gases or liquids) and radiation (as by means of radiant-heat energy).

HEAT TRANSFER *is always from a warmer to a colder place.*



HEAVY HYDROGEN

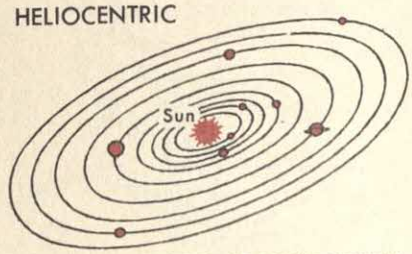
heavy hydrogen \'hev-ē 'hī-drə-jən\
Another name for deuterium. See *deuterium*.

heavy water \'hev-ē 'wȯt-ər\
CHEMISTRY. Water in which deuterium atoms take the place of

ordinary hydrogen atoms. Heavy water has approximately the same chemical properties as ordinary water but is somewhat denser. It is found in water as one part in approximately 6,000 parts. Its chemical name is deuterium oxide.

HEAVY WATER is used as a moderator to slow down neutrons in nuclear reactors.

HELIOCENTRIC



(MODEL OF SOLAR SYSTEM)

hectometer \'hek-tə-ˌmēt-ər\ *n.*

MATHEMATICS. A unit of length in the metric system equal to 100 meters, or 328.08 feet.

Ten decameters are equal to one HECTOMETER.

heliocentric \ˌhē-lē-ō-'sen-trik\ *adj.*

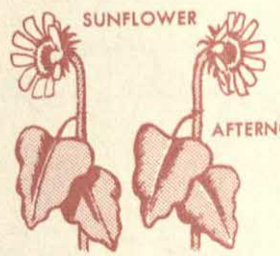
ASTRONOMY. Related to, or measured from, the sun's center; also, having the sun as a center.

In a HELIOCENTRIC *model of the solar system, the sun is at the center and the planets revolve around it.*

heliodyne \'hē-lē-ə-ˌdīn\ *n.*

ASTRONAUTICS. A spacecraft that can use the sun's heat to help manufacture its own fuel.

The HELIODYNE *is a spacecraft of the future.*



HELIOTROPISM

heliotropism \ˌhē-lē-'ä-trə-piz-əm\ *n.*

BOTANY. The curvature or turning of certain plants or plant parts in response to the stimulus of sunlight; also, a form of phototropism in which sunlight is the stimulus.

The daily turning of the head of a sunflower is an example of HELIOTROPISM.

helium \'hē-lē-əm\ *n.*

AERONAUTICS and CHEMISTRY. A very light, colorless, gaseous element. Because it is less dense than air and will not burn or explode, helium is used in blimps and dirigibles. Symbol, He; atomic number, 2; atomic weight, 4.0026.

The nucleus of an atom of HELIUM, *known as an alpha particle, has two protons and two neutrons and is useful in experimental work with radioisotopes.*

HELIX

helix \'hē-liks\ *n.*

1. MATHEMATICS. A curve that intersects the elements of a cylindrical or conical surface at a constant angle. 2. PHYSICS. A cylindrical coil of wire, such as a solenoid.

Stripes on a barber pole or the threads of a bolt form a circular HELIX.

hematin \\'hem-ət-ən\\ *n.*

PHYSIOLOGY. An insoluble, nonprotein iron complex that is a constituent of hemoglobin; the colored portion of the hemoglobin molecule.

When hemoglobin from red corpuscles is broken down, most of the HEMATIN *is converted to bile pigment.*

hematite \\'hem-ə-ˌtīt\\ *n.*

EARTH SCIENCE. Fe_2O_3. A mineral, iron oxide, the most abundant and important ore of iron.

Rich deposits of HEMATITE *are found near Birmingham, Alabama.*

HEMISPHERE

hemisphere \\'hem-ə-ˌsfi(ə)r\\ *n.*

1. EARTH SCIENCE. Either of two halves of the earth formed by an imaginary plane passing through the earth's center. 2. MATHEMATICS. One of the two equal parts of a sphere obtained by cutting the sphere by a plane that passes through the center. 3. ANATOMY. Either half of the lateral halves of the cerebrum or cerebellum.

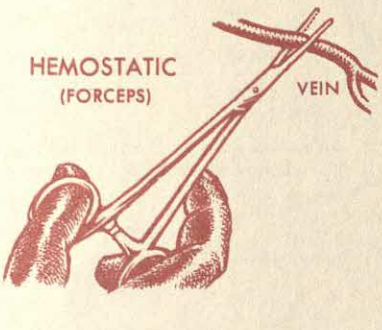
If we consider the earth a sphere, the Northern HEMISPHERE *is divided from the Southern Hemisphere by the equator.*

hemoglobin \\'hē-mə-ˌglō-bən\\ *n.*

ANATOMY and ZOOLOGY. The oxygen-carrying pigment in the red corpuscles, composed of the nonprotein hematin and the protein globin.

Combined with oxygen in the lungs, HEMOGLOBIN *becomes bright red in color.*

HEMOSTATIC (FORCEPS)



hemorrhage \\'hem-(ə-)rij\\ *n.*

MEDICINE. A rapid loss of blood from the vessels, resulting from broken or cut arteries, veins or capillaries.

Treatment after a HEMORRHAGE *may include a blood transfusion.*

hemostatic \\ˌhē-mə-'stat-ik\\ *adj.*

MEDICINE. Referring to any substance used to stop a flow of blood by constricting blood vessels or by starting the clotting process; also, referring to an instrument used to clamp a bleeding vessel.

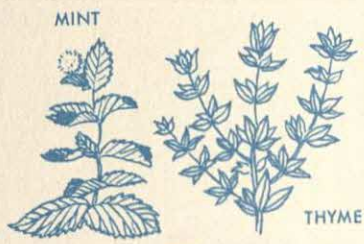
HEMOSTATIC *forceps are often used to stop bleeding from large vessels during surgery.*

hemotoxin \ˈhē-mō-ˌtäk-sən\ *n.*
MEDICINE and PHYSIOLOGY. Any substance capable of destroying blood cells.

The HEMOTOXIN *in cobra venom will dissolve red corpuscles.*

henry \ˈhen-rē\ *n.*
PHYSICS. An electrical unit equal to 1×10^9 cgs units of inductance.

Because the HENRY *is a relatively-large unit, the millihenry, 1/1000 as large, is commonly used.*



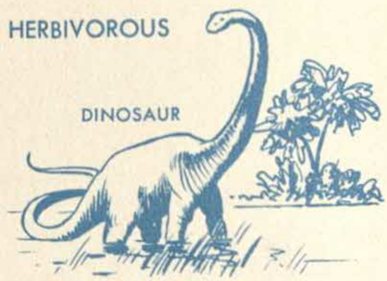
HERB

Henry's law \ˈhen-rēz ˈlȯ\
CHEMISTRY and PHYSICS. A law stating that the weight of a gas dissolved in a given volume of liquid is directly proportional to the pressure of that gas on the surface of the liquid.

HENRY'S LAW *does not apply strictly to a gas that reacts with the liquid in which it dissolves.*

herb \ˈ(h)ərb\ *n.*
BOTANY. A flowering plant that has a soft stem without woody tissues.

An HERB *is often valuable for its medicinal or flavoring properties.*

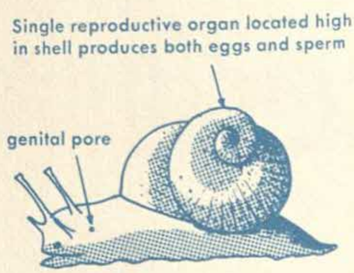


herbivorous \ˌ(h)ər-ˈbiv-ə-rəs\ *adj.*
ZOOLOGY. Referring to animals that feed only on plants.

Many of the large, prehistoric animals were HERBIVOROUS.

heredity \hə-ˈred-ət-ē\ *n.*
BIOLOGY. In plants and animals, the transmission through reproduction of factors that cause an offspring to resemble its parent or parents.

The characteristics of an organism result from both HEREDITY *and environment.*



HERMAPHRODITIC

hermaphroditic \(ˌ)hər-ˌmaf-rə-ˈdit-ik\ *adj.*
BIOLOGY. Pertaining to a living organism, either an animal or a plant, that has both male and female reproductive systems or organs in one individual.

A HERMAPHRODITIC *animal, such as a snail or an earthworm, produces both eggs and sperm.*

hermetic \(ˌ)hər-ˈmet-ik\ *adj.*
Referring to airtightness or to airtight sealing.

A vacuum chamber requires an effective HERMETIC *seal.*

herpetology \\ˌhər-pə-ˈtäl-ə-jē\\ *n.*
ZOOLOGY. A branch of zoology concerned with the study of reptiles, such as snakes and turtles, and of amphibians, such as frogs and toads. It is sometimes defined to include only the study of reptiles.

An investigator doing research in HERPETOLOGY *may study the structures of such prehistoric reptiles as the dinosaurs.*

HETEROPHYTE

heterogeneous \\ˌhet-ə-rə-ˈjē-nē-əs\\ *adj.*
CHEMISTRY. Pertaining to a mixture of unlike substances with clear and distinct surfaces or boundaries separating them; also, referring to the chemical or physical condition within a container or system in which a reversible reaction is at equilibrium.

The condition existing in a container holding a saturated salt solution with salt resting on the bottom is described as HETEROGENEOUS.

heterophyte \\ˈhet-ə-rə-ˌfit\\ *n.*
BOTANY. A plant that does not carry on photosynthesis and that obtains its foods from other living and nonliving organisms.

The mushroom is a HETEROPHYTE *that obtains nourishment from dead leaves and other decaying organic matter.*

HETEROTROPH

heterotroph \\ˈhet-ə-rə-ˌträf\\ *n.*
BIOLOGY. An organism that requires complex organic compounds of carbon and nitrogen to maintain life, as opposed to organisms that manufacture such compounds through photosynthesis; see *autotroph.*

All higher animals are HETEROTROPHS, *since they feed on plants or on other animals.*

heterozygote \\ˌhet-ə-rō-ˈzī-ˌgōt\\ *n.*
BIOLOGY. An animal or plant that has inherited from its parents unlike genes that control one or more characteristics.

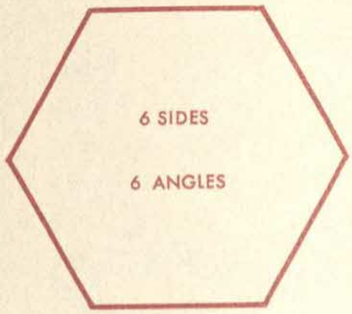
A HETEROZYGOTE *may have both a dominant and a recessive gene for a particular trait.*

heuristic \\hyü-ˈris-tik\\ *adj.*
Referring to an assumption, something that is unproved and even dubious, but that is useful as a stimulus to further argument or research.

A HEURISTIC *procedure starts with persuasion and then seeks proof.*

hexagon \\'hek-sə-ˌgän\\ *n.*
MATHEMATICS. A polygon having six sides.

A regular HEXAGON *has six equal sides and angles.*



HEXAGON

hexapod \\'hek-sə-ˌpäd\\ *n.*
ZOOLOGY. One of the class Hexapoda or Insecta; a true insect having three pairs of legs and three main body divisions (head, thorax and abdomen).

A housefly or a bee is an example of a HEXAPOD, *but a spider or tick is not.*

hibernate \\'hī-bər-ˌnāt\\ *v.*
ZOOLOGY. To remain inactive during the winter months, as do some mammals, amphibians and reptiles; also, to become inactive during a phase of development, as some insects.

When animals HIBERNATE, *their body temperatures are lower, and their rates of heartbeat and breathing decrease.*

high \\'hī\\ *n.*
EARTH SCIENCE. A region of high atmospheric pressure; an anticyclone.

The wind moves in a clockwise direction around a HIGH *in the Northern Hemisphere and in a counterclockwise direction around a high in the Southern Hemisphere.*

HOUSEFLY

HEXAPOD

high-fidelity \\'hī fə-'del-ət-ē\\ *adj.*
ENGINEERING and PHYSICS. Pertaining to a system that reproduces sound having characteristics nearly the same as the original sound; also, referring to the sound reproduced.

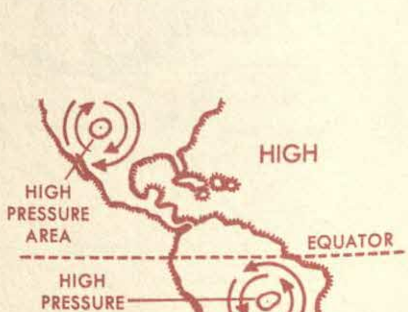
The HIGH-FIDELITY *reproduction of a concert gives the listener the effect of listening directly to the orchestra.*

high-frequency \\'hī 'frē-kwən-sē\\ *adj.*
ENGINEERING. In radio communication, referring to any frequency within a range of 3 to 30 megacycles per second.

HIGH-FREQUENCY *waves have short wavelengths (the higher the frequency, the shorter the wavelength).*

high-octane gasoline \\ˌhī-'äk-ˌtān ˌgas-ə-'lēn\\
CHEMISTRY. A gasoline that has an octane number higher than 100. One example of a compound often used in such gasoline is the hydrocarbon triptane, with an octane number of 125; see *octane rating.*

The use of HIGH-OCTANE GASOLINE *provides increased power in engines.*

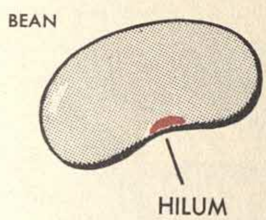


HIGH

high tide \\'hī 'tīd\\

EARTH SCIENCE. The highest elevation of each rising tide; also called flood tide.

The times of HIGH TIDE *vary from day to day.*



hilum \\'hī-ləm\\ *n.*

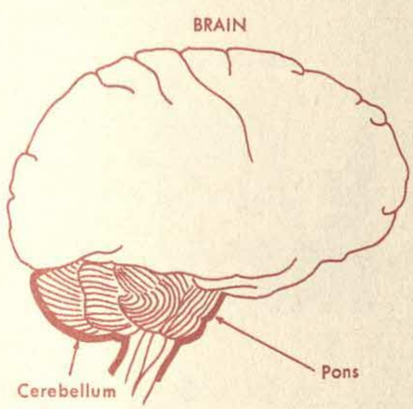
BOTANY. The scar on a seed caused by the separation of the seed from its stalk.

The HILUM *is easily observed on seeds that develop in a pod, such as beans and peas.*

hindbrain \\'hīn(d)-ˌbrān\\ *n.*

ANATOMY. The embryonic nervous tissue that develops into the cerebellum, the pons and the medulla oblongata.

HINDBRAIN *is sometimes used to refer specifically to the cerebellum and the pons.*



HINDBRAIN

histamine \\'his-tə-ˌmēn\\ *n.*

MEDICINE and PHYSIOLOGY. $C_3H_3N_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$. An amine found in all animal and plant tissue that dilates the capillaries, lowers the blood pressure and stimulates gastric secretions; also, a synthetic drug with similar properties.

HISTAMINE *is sometimes used by physicians in testing stomach secretions.*

histogram \\'his-tə-ˌgram\\ *n.*

MATHEMATICS. A representation of frequency distributions on a graph by adjacent bars whose lengths are proportional to the mathematical quantities they represent and whose widths represent equal intervals of the variable under study.

A HISTOGRAM *may be used in the statistical analysis of research results.*

histology \\his-'täl-ə-jē\\ *n.*

BIOLOGY and MEDICINE. The microscopic study of the structure, composition and function of plant and animal tissues.

The techniques of HISTOLOGY *are used in medical practice to help diagnose certain diseases.*

HOARFROST

hoarfrost \\'hō(ə)r-ˌfrȯst\\ *n.*

EARTH SCIENCE. Small, silvery needles or crystals of ice that form on the ground and on objects near the ground when the temperature is below 0° C. or 32° F.

HOARFROST *may consist partly of frozen dew and partly of ice crystals formed directly from water vapor.*

homeostasis \ˌhō-mē-ō-'stā-səs\ *n.*
PHYSIOLOGY and ZOOLOGY. A constant tendency toward stability, or uniformity, of the normal internal environment, or fluids in the tissues, of an organism.

HOMEOSTASIS *results from the maintenance of chemical equilibrium within body tissues.*

homogeneous \ˌhō-mə-'jē-nē-əs\ *adj.*
1. CHEMISTRY. Having uniform composition, both chemically and physically; also, consisting of a single phase. 2. MATHEMATICS. Having all the terms of the same degree, as a polynomial, with respect to the variables in it. 3. BIOLOGY. Describing organisms having similar structures because of descent from a common ancestor.

A sugar is a HOMOGENEOUS *substance.*

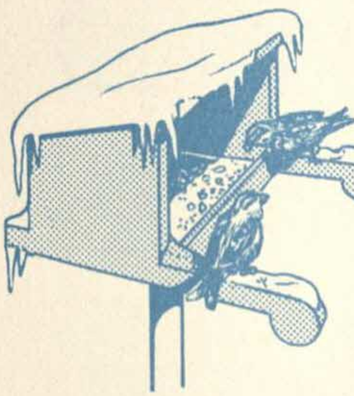
homogenize \hō-'mäj-ə-ˌnīz\ *v.*
To form by mixing and by breaking up the fine particles or globules of a liquid within a liquid.

Dairies HOMOGENIZE *milk to prevent separation of the cream from the milk.*

homoiothermic \hō-ˌmȯi-ə-'thər-mik\ *adj.*
ZOOLOGY. Referring to animals that maintain a body temperature different from the temperature of the air or water around them; warm-blooded.

Birds and mammals are HOMOIOTHERMIC.

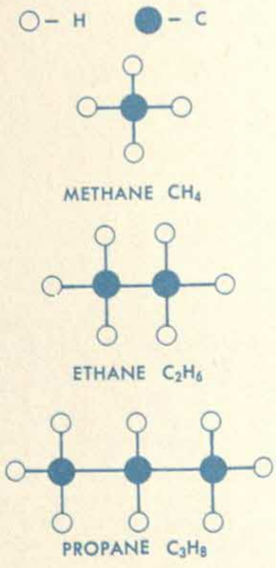
Birds keep warm in winter



HOMOIOTHERMIC

homologous series \hō-'mäl-ə-gəs 'si(ə)r-(ˌ)ēz\
CHEMISTRY. A series of carbon compounds having the same general formula in which each member differs from the preceding member by the same group, such as CH_2.

Methane, ethane and propane are part of a HOMOLOGOUS SERIES *called the paraffin group.*



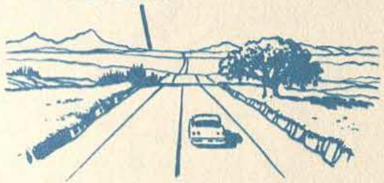
HOMOLOGOUS SERIES

homozygote \ˌhō-mō-'zī-ˌgōt\ *n.*
BIOLOGY. An animal or plant that has inherited from its parents one or more pairs of like, or identical, genes.

An offspring of two identically-purebred animals is a HOMOZYGOTE *in respect to all traits.*

horizon \hə-'rīz-ᵊn\ *n.*
1. EARTH SCIENCE. The line or circle that appears to be the boundary between the earth and the sky; also, the surface be-

tween two rock units or between two soil layers. 2. ASTRONOMY. The great circle on the celestial sphere halfway between the zenith and the nadir.



The HORIZON *as seen by a person at sea is a complete circle, but on land it is usually broken by surface obstructions.*

hormone \'hȯr-ˌmōn\ *n.*

1. ANATOMY. In animals, a chemical substance that is formed by endocrine glands and secreted into the body fluids, having specific effects on other organs. 2. BOTANY. A similar chemical agent in plants.

One HORMONE, *insulin, regulates the metabolism of carbohydrates.*

horn \'hȯ(ə)rn\ *n.*

1. ZOOLOGY. A bony, pointed growth on the head of some hoofed animals, occurring more often in the male. 2. EARTH SCIENCE. A high mountain peak with steep sides formed by cirques on at least two sides; also, a cape or headland.

A HORN *may be a solid bony growth or a special outgrowth of the epidermis around a bony inner core.*

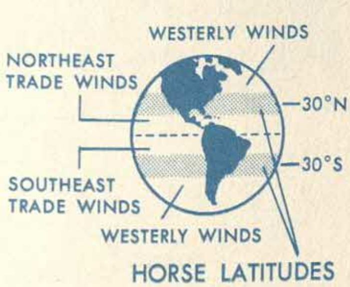
horse latitudes \'hȯ(ə)rs 'lat-ə-ˌt(y)üdz\

EARTH SCIENCE. Belts of high-pressure areas that stretch across the temperate zones. They lie approximately 30 degrees north and 30 degrees south of the equator between the trade winds and the prevailing westerlies.

Prolonged periods of light winds or calm air occur in the HORSE LATITUDES.

horsepower \'hȯr-ˌspau̇(-ə)r\ *n.*

PHYSICS. A unit of power, or rate of work, equal to 550 foot-pounds per second (33,000 foot-pounds per minute), or 746 watts.



Historically, HORSEPOWER *was based upon the rate at which a horse could do work.*

horticulture \'hȯrt-ə-ˌkəl-chər\ *n.*

BOTANY. A branch of agriculture dealing with the growing of flowers, fruits and vegetables.

Landscape gardening is sometimes considered a part of HORTICULTURE.

host \'hōst\ *n.*
BIOLOGY. A plant or animal that is a source of nourishment for a parasite.

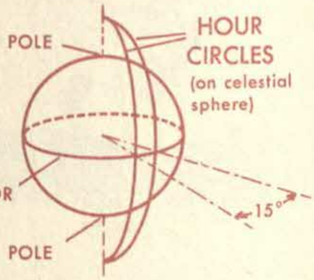
Some parasites live on the surface of the HOST, *while others live internally.*

hour angle \'au̇(-ə)r 'aŋ-gəl\
ASTRONOMY. The angular distance of a star or other object measured along the celestial equator westward from the celestial meridian to the hour circle of the star.

The HOUR ANGLE *of a celestial object is equal to the sidereal time minus the right ascension of the object.*

hour circles \'au̇(-ə)r 'sər-kəlz\
ASTRONOMY. Circles on the celestial sphere that pass through the celestial poles. They correspond to meridians on the terrestrial sphere and are often used in determining the position of stars.

HOUR CIRCLES *are at right angles to the celestial equator.*



hull \'həl\ *n.*
1. BOTANY. The outer covering, usually a husk or a shell, of a seed or a fruit. 2. AERONAUTICS and ENGINEERING. The body or the frame of an airplane or a ship.

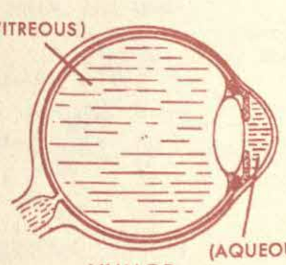
The HULL *of cereal grains, such as wheat and rice, contains most of the vitamin content found in those foods.*

humidity \hyü-'mid-ət-ē\ *n.*
EARTH SCIENCE. The water vapor content, or moisture, in the atmosphere, usually calculated as relative humidity or as absolute humidity.

The absolute HUMIDITY *of air saturated with water vapor at room temperature is about 20 grams per cubic meter of air.*

humor \'hyü-mər\ *n.*
PHYSIOLOGY. Any fluid or semifluid substance in the body.

Light rays are refracted as they enter and leave the eye's aqueous HUMOR.



humus \'hyü-məs\ *n.*
EARTH SCIENCE. Dark-colored organic material in the soil, consisting of decomposed and partly-decomposed vegetable and animal matter.

The HUMUS *in soil is one of the earth's most valuable natural resources.*

hundredweight \'hən-drə-ˌdwāt\ *n.*

MATHEMATICS. A unit of weight equal to 100 pounds, or 45.36 kilograms, in the United States and to 112 pounds, or 50.80 kilograms, in England.

The metric HUNDREDWEIGHT *is equal to 50 kilograms.*

hurricane \'hər-ə-ˌkān\ *n.*

EARTH SCIENCE. A severe windstorm or tropical cyclone having a diameter of from 50 to 1,000 miles; a wind of force 12 on the Beaufort scale (speed greater than 72 miles per hour).

A HURRICANE *is a storm that frequently originates in the West Indies in August, September or October.*

hybrid \'hī-brəd\ *n.*

BIOLOGY. An offspring resulting from the crossing of parents differing in hereditary traits, the offspring often developing characteristics different from those of either parent.

A HYBRID *that is larger and more vigorous than either parent is referred to as having hybrid vigor.*

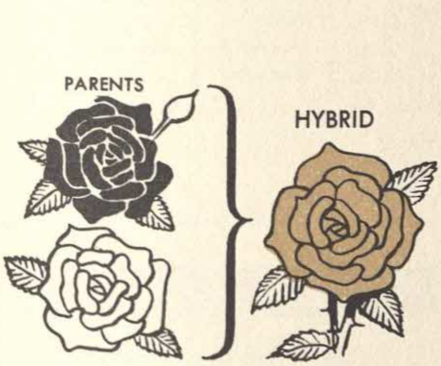
hybrid computer \'hī-brəd kəm-'pyüt-ər\

MATHEMATICS. A computer that combines within itself the functions of both analog and digital computers.

A HYBRID COMPUTER *can convert data from analog to digital form and back again.*

hybridization \ˌhī-brəd-ə-'zā-shən\ *n.*

BIOLOGY. The process of crossbreeding two individuals of unlike genetic makeup, thus producing a hybrid.



If during HYBRIDIZATION *two hybrids are crossed, the offspring may resemble both parents, one parent or neither parent in some specific trait or characteristic.*

hydrate \'hī-ˌdrāt\ *n.*

CHEMISTRY. A compound containing combined water of crystallization in a specific ratio by weight and by definite formula.

A HYDRATE *from which water has been removed is said to be anhydrous.*

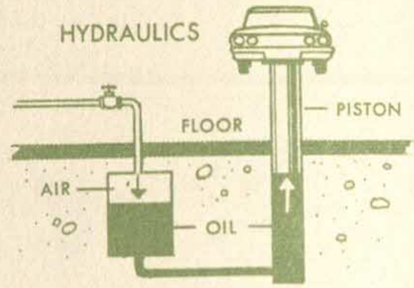
hydrated ion \'hī-ˌdrāt-əd 'ī-ən\

CHEMISTRY. In a solute, an ion that has a strong attraction for a water molecule and that has become attached to it.

The hydronium ion, H_3O^+, is a HYDRATED ION *resulting from the combination of a hydrogen ion, H^+, and a molecule of water, H_2O.*

hydration \hī-'drā-shən\ *n.*
CHEMISTRY. A chemical process in which a compound combines with water to form a hydrate.

Blue vitriol is a well-known salt formed by the HYDRATION *of copper sulphate.*



hydraulics \hī-'drȯ-liks\ *n.*
ENGINEERING. A branch of fluid mechanics concerned with the behavior, properties and uses of liquids in motion.

The principles of HYDRAULICS *are utilized in civil, mechanical and chemical engineering.*

hydride \'hī-ˌdrīd\ *n.*
CHEMISTRY. A binary compound that is composed of hydrogen and another element, such as hydrogen sulfide, H_2S, or water, H_2O.

A HYDRIDE *may be covalent, saltlike or metallic.*

hydrocarbons \ˌhī-drə-'kär-bənz\ *n.*
CHEMISTRY. Compounds containing only the elements hydrogen and carbon, such as methane, CH_4, and acetylene, C_2H_2.

All HYDROCARBONS *are combustible, and many of them are used as fuels.*

HYDROCARBONS
(Examples)

CH_4	Methane	Natural gas
C_2H_6	Ethane	
C_3H_8	Propane	
C_4H_{10}	Butane	Naphtha
C_5H_{12}	Pentane	
C_6H_{14}	Hexane	
C_7H_{16}	Heptane	Gasoline
C_8H_{18}	Octane	
C_9H_{20}	Nonane	
$C_{10}H_{22}$	Decane	Kerosene
$C_{11}H_{24}$	Undecane	
$C_{12}H_{26}$	Dodecane	

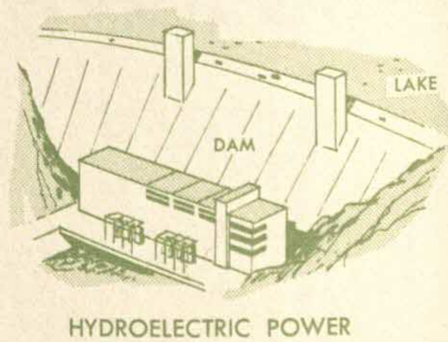
hydrochloric acid \ˌhī-drə-'klōr-ik 'as-əd\
1. CHEMISTRY. A colorless, pungent-smelling liquid formed by the solution of hydrogen chloride, HCl, in water, yielding hydronium ions, H_3O^+, and chloride ions, Cl^-. 2. PHYSIOLOGY. A highly-dilute acid that is found in the gastric juice of the stomach.

HYDROCHLORIC ACID *is used industrially for cleaning metals and in the preparation of chlorides.*

hydrodynamics \ˌhī-(ˌ)drō-(ˌ)dī-'nam-iks\ *n.*
ENGINEERING. A branch of science dealing with fluids in motion; see *hydraulics.*

hydroelectric power \ˌhī-drō-i-'lek-trik 'pau̇(-ə)r\
PHYSICS. Electricity generated in a turbine that is turned by flowing or falling water.

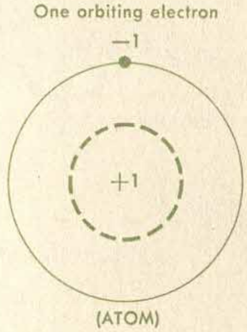
The amount of HYDROELECTRIC POWER *produced by a water turbine depends on the pressure and the volume of the water that flows into the turbine.*



HYDROELECTRIC POWER

hydrofoil \ˈhī-drə-ˌfȯil\ *n.*
ENGINEERING and PHYSICS. A platelike surface attached below the hull of a boat or seaplane. It contacts the water and provides an increase in hydrodynamic lift to increase the speed of the boat or seaplane.

A HYDROFOIL *functions in water somewhat as an airfoil functions in air.*



HYDROGEN

hydroforming \ˈhī-drə-ˌfȯr-miŋ\ *n.*
CHEMISTRY. The conversion of straight-chain hydrocarbons obtained from petroleum into ring compounds by heating them with hydrogen in the presence of a catalyst.

The gasoline produced by HYDROFORMING *has very good antiknock properties.*

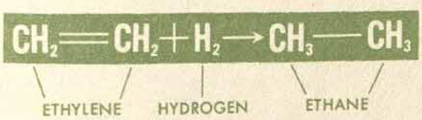
hydrogen \ˈhī-drə-jən\ n.
CHEMISTRY. A colorless, odorless, chemical element, gaseous at ordinary temperature and pressure and chemically very active, combining with all elements except the inert gases. It is found in water, all organic matter and all acids, and it contains three isotopes: protium, H^1, deuterium, H^2, and tritium, H^3. Symbol, H; atomic number, 1; atomic weight, 1.00797.

HYDROGEN *is the least dense of all elements.*

hydrogenation \(ˌ)hī-ˌdräj-ə-ˈnā-shən\ *n.*
CHEMISTRY. The conversion of those liquid oils that are unsaturated hydrocarbons to saturated hydrocarbons by combining hydrogen with the unsaturated compounds, using nickel as a catalyst.

Vegetable shortening and oleomargarine are often made by the HYDROGENATION *of cottonseed oil.*

HYDROGENATION



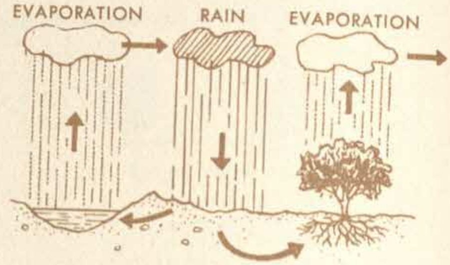
hydrogen-ion concentration \ˈhī-drə-jən ˈī-ən ˌkän(t)-sən-ˈtrā-shən\
CHEMISTRY. The concentration of hydrogen ions in a solution; also, a measure of the degree of acidity of a solution, generally expressed as pH, where $pH = \log \frac{1}{[H+]}$.

A tenth-normal solution of hydrochloric acid has a high HYDROGEN-ION CONCENTRATION.

hydrogen peroxide \ˈhī-drə-jən pə-ˈräk-ˌsīd\
CHEMISTRY. H_2O_2. A compound of hydrogen and oxygen that is a colorless, sirupy liquid. In dilute form, it is used as an anti-

septic and as a bleaching agent and, in concentrated form, as an oxidizing agent in rocket fuels.

At high temperatures, a concentrated solution of HYDROGEN PEROXIDE *decomposes with explosive rapidity.*



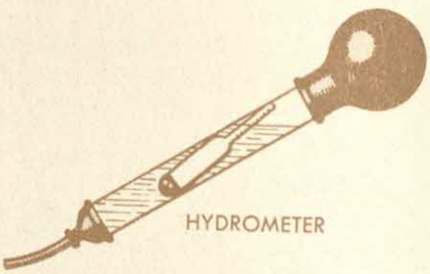
HYDROLOGIC CYCLE

hydrologic cycle \\ˌhī-drə-ˈläj-ik ˈsī-kəl\\
EARTH SCIENCE. The circulation of water as it evaporates from streams, lakes, oceans and land surfaces, condenses in the atmosphere, falls to the earth as rain, sleet or snow and drains along or into the ground or into bodies of water where evaporation again takes place; also called water cycle.

Water taken into plants and animals reenters the HYDROLOGIC CYCLE *when respired or excreted by animals or when transpired by plants.*

hydrolysis \\hī-ˈdräl-ə-səs\\ *n.*
CHEMISTRY. The reaction of water with another compound, such as a salt, resulting in the formation of a weak acid or a weak base; also, the reaction of water with another compound, such as sucrose, to produce two simple sugars, glucose and fructose.

Glucose is produced commercially by the HYDROLYSIS *of starch.*

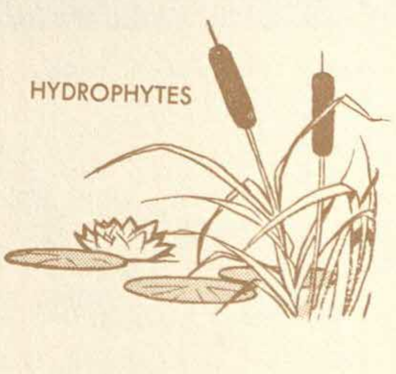

HYDROMETER

hydrometer \\hī-ˈdräm-ət-ər\\ *n.*
ENGINEERING and PHYSICS. An instrument used to measure the specific gravity of liquids; a device that floats upright in liquids at a depth dependent upon the density of the liquid.

The HYDROMETER *is widely used in determining the condition of the antifreeze solution in the radiator of an automobile.*

hydronium ion \\hī-ˈdrō-nē-əm ˈī-ən\\
CHEMISTRY. H_3O^+. A combination of a hydrogen ion and a water molecule, found in acid aqueous solutions; a hydrated proton.

The symbol for the hydrogen ion, H^+, is often used in equations instead of the symbol for the HYDRONIUM ION.

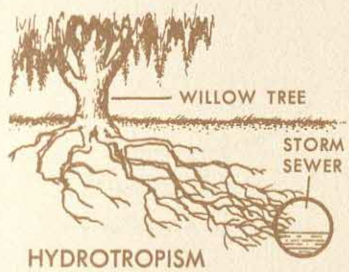
HYDROPHYTES


hydrophytes \\ˈhī-drə-ˌfīts\\ *n.*
BOTANY. Plants that grow in water or in very wet soil.

Cattails and water lilies are HYDROPHYTES.

hydroponics \ˌhī-drə-'pän-iks\ *n.*
BOTANY. The growing of plants in either sand or solution, the necessary minerals being provided in the form of dissolved inorganic salts; soilless gardening.

HYDROPONICS, *used mainly in plant experimentation, has also been used in agriculture on a limited scale.*



HYDROTROPISM

hydrosphere \'hī-drə-ˌsfi(ə)r\ *n.*
EARTH SCIENCE. The part of the earth that contains, or is covered by, water, including ground water, lakes, rivers, seas and atmospheric water vapor; also, sometimes, the earth's envelope of water vapor.

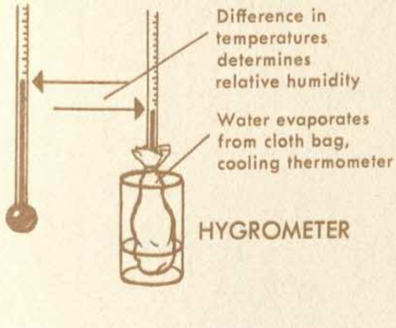
The HYDROSPHERE *includes the portions of the atmosphere and the lithosphere that contain water.*

hydrostatics \ˌhī-drə-'stat-iks\ *n.*
PHYSICS. The branch of mechanics concerned with water and other liquids not in motion, dealing principally with the pressure and equilibrium of liquids.

The design of an underwater tunnel depends heavily on HYDROSTATICS.

hydrotropism \hī-'drä-trə-ˌpiz-əm\ *n.*
BIOLOGY. The response of an organism to the stimulus of water or to moisture in the air.

The growth of a plant root toward wet soil demonstrates HYDROTROPISM.



HYGROMETER

hydroxide \hī-'dräk-ˌsīd\ *n.*
CHEMISTRY. An inorganic compound containing the hydroxyl radical OH^-; also, the anion OH^- itself. A solution of hydroxide has a bitter taste, feels slippery and turns red litmus paper blue.

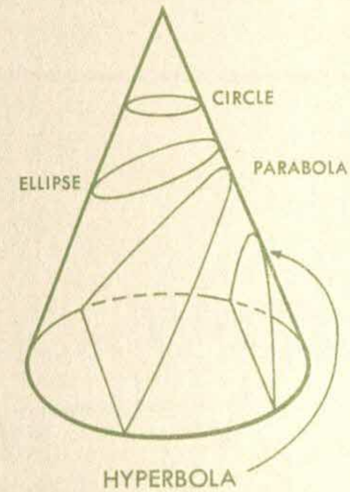
The reaction of a HYDROXIDE *with an oxide of a nonmetal produces water and a salt.*

hygrometer \hī-'gräm-ət-ər\ *n.*
ENGINEERING and PHYSICS. An instrument that measures the relative or absolute humidity of air or other gases.

The most common kind of HYGROMETER *for measuring relative humidity is the wet- and dry-bulb thermometer, or psychrometer.*

hygroscopic \ˌhī-grə-'skäp-ik\ *adj.*
CHEMISTRY. Readily absorbing and retaining moisture from the atmosphere.

A HYGROSCOPIC *salt, such as calcium chloride, is used to reduce dust on an unpaved road.*

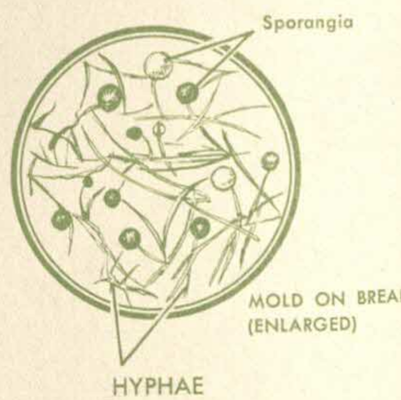


hyoid \'hī-ˌȯid\ *n.*
ANATOMY. A U-shaped bone located at the base of the tongue. The muscles of the tongue are attached to it, and it is suspended by ligaments from the styloid processes of the temporal bones.

The HYOID *may be felt under the chin, just above the larynx.*

hyperbola \hī-'pər-bə-lə\ *n.*
MATHEMATICS. A conic section having two branches and whose eccentricity is greater than one; also, the set of points the difference of whose distances from two fixed points, called foci, is a constant.

A HYPERBOLA, *like other conic sections, is formed by the intersection of a cone and a plane.*



hypersonic speed \ˌhī-pər-'sän-ik 'spēd\
ASTRONAUTICS. Speed that is five or more times greater than the speed of sound (Mach number of 5 or more).

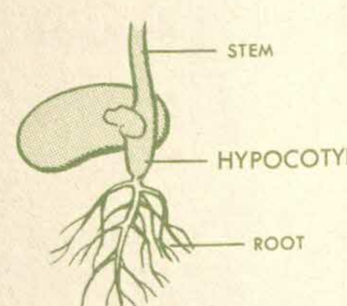
Long, slender bodies and thin airfoils are characteristic of aircraft that fly at a HYPERSONIC SPEED.

hypertension \ˌhī-pər-'ten-chən\ *n.*
MEDICINE and PHYSIOLOGY. A persistent, abnormal elevation of arterial blood pressure, especially the diastolic blood pressure; also, any abnormally-high tension.

HYPERTENSION *may accompany diseases of the kidneys.*

hyphae \'hī-(ˌ)fē\ *n.*
BIOLOGY. The threadlike, colorless filaments that make up the mycelium, or plant body, of a fungus.

The fuzzy growth we see on stale bread is a tangle of HYPHAE *produced by the common mold, Rhizopus nigricans.*



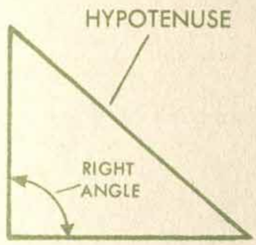
hypocotyl \'hī-pə-ˌkät-ᵊl\ *n.*
BOTANY. The part of the embryo of a seed that develops into the stem below the cotyledons.

The root system develops from the lower end of a HYPOCOTYL.

hypotension \ˌhī-pō-ˈten-chən\ *n.*
MEDICINE and PHYSIOLOGY. Unusually low blood pressure.

HYPOTENSION *may be the result of shock.*

hypotenuse \hī-ˈpät-ᵊn-ˌ(y)üs\ *n.*
MATHEMATICS. In a right triangle, the side opposite the right angle.



The HYPOTENUSE *is always the longest side of a right triangle.*

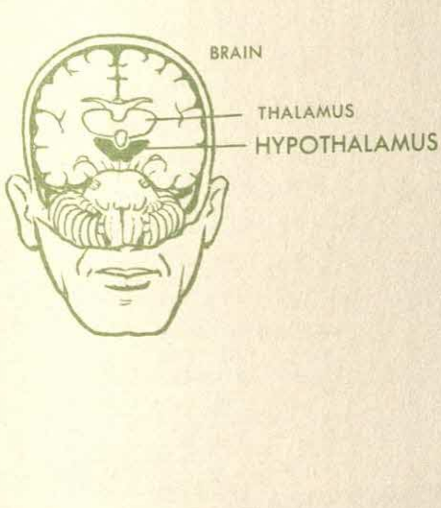
hypothalamus \ˌhī-pō-ˈthal-ə-məs\ *n.*
ANATOMY and ZOOLOGY. The part of the cerebrum below the thalamus that exerts control over emotional responses, temperature, water balance, appetite and fat metabolism.

Electrical stimulation of the HYPOTHALAMUS *of an animal results in sleep.*

hypothesis \hī-ˈpäth-ə-səs\ *n.*
1. MATHEMATICS. The conditional part of a statement of implication; also, the set of conditions of a theorem that are given as assumed or known. 2. Something held to be true because it seems to explain adequately the available data or observations.

A statement of implication is false if, and only if, the HYPOTHESIS *is true and the conclusion is false.*

hypoxia \hip-ˈäk-sē-ə\
PHYSIOLOGY. Oxygen deficiency in the blood, cells and tissues, caused at high altitude by low oxygen content in the atmosphere or by low pressure.



The danger of HYPOXIA *has been minimized in high-flying aircraft by the use of pressurized cabins and auxiliary oxygen supplies.*

hysteresis \ˌhis-tə-ˈrē-səs\ *n.*
PHYSICS. A lagging effect when a force upon a body is changed, seeming to be the result of internal friction; also, the effect in iron or steel within a magnetic field produced by a rapidly-alternating current. Residual magnetism in the iron or steel is reduced by the reversing current with each change of direction, the energy used in the process appearing as heat.

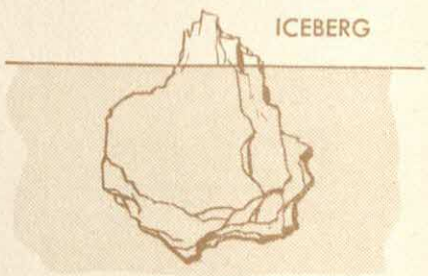
To increase efficiency, the core of a transformer should be made from an iron alloy having low loss by HYSTERESIS.

I

ice age \'īs 'āj\

EARTH SCIENCE. One of the prehistoric periods of time when glaciers covered large portions of continental land masses. Ice Age refers specifically to the Pleistocene epoch of geologic time, the most recent ice age.

The glaciers now present in Greenland and Antarctica are similar to those that covered greater areas during an ICE AGE.



iceberg \'īs-ˌbərg\ *n.*

EARTH SCIENCE. A large mass of ice floating in the ocean; frequently, large blocks of ice that have broken away from a glacier and fallen into the sea.

In salt water, an ICEBERG *floats with about 1/8 of its bulk above water and 7/8 below the water surface.*

ice sheet \'īs 'shēt\

EARTH SCIENCE. A glacier or a relatively-thick covering of ice on land areas. In a localized area, it is called an ice cap.

Because an ICE SHEET *covers practically all of Greenland, the area is a cold desert.*

SOUTHERN LIMITS OF ICE SHEETS IN NORTH AMERICA

ich \'ik\ *n.*

MEDICINE and ZOOLOGY. A skin disease of freshwater fish caused by the invasion of a ciliated protozoan, *Ichthyophthirius multifiliis;* also spelled ick.

Aquarium fish often get ICH.

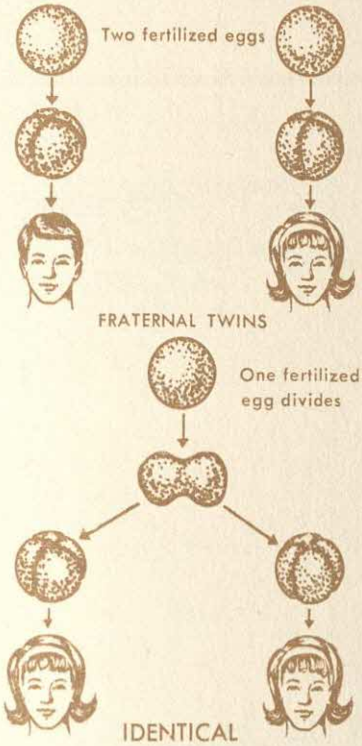
ichthyology \ˌik-thē-'äl-ə-jē\ *n.*

ZOOLOGY. The science of the groups, forms, habits and development of fish.

Field work in ICHTHYOLOGY *includes the determination of fish populations in lakes, rivers and seas.*

identical twins \ī-'dent-i-kəl 'twinz\

Twins that result when one fertilized egg divides and separates



IDENTICAL TWINS

into two cells that then develop into individuals with the same hereditary traits.

IDENTICAL TWINS are studied by psychologists to learn more about the effects of environment on personality.

igneous rock \'ig-nē-əs 'räk\

EARTH SCIENCE. Rock formed when hot, molten rock material, called magma, cools and solidifies within or on the earth.

The faster an IGNEOUS ROCK cools, the smaller its crystals are and the finer its texture.

ignition \ig-'nish-ən\ *n.*

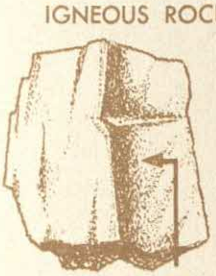
1. CHEMISTRY. Heating a substance to a high temperature in the presence of air, resulting in the formation of oxides or other stable compounds. 2. ENGINEERING. Commonly, the electrical switch that is used to start a gasoline engine. 3. The act of igniting or setting on fire; also, the process of starting combustion in a furnace, engine or rocket.

One of the steps in analyzing wood for its mineral content is the IGNITION of a sample to remove the elements carbon and hydrogen.

IGY

Abbreviation for International Geophysical Year. See *International Geophysical Year.*

IGNEOUS ROCK



ileum \'il-ē-əm\ *n.*

ANATOMY and ZOOLOGY. The last and longest part of the small intestine, extending from the jejunum to the large intestine.

Absorption of food substances takes place in the ILEUM, as well as in the other divisions of the small intestine.

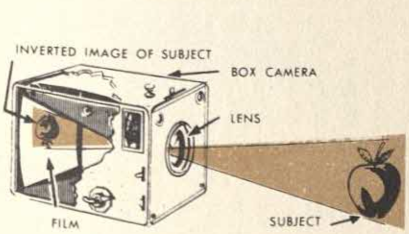
illumination \il-ˌü-mə-'nā-shən\ *n.*

PHYSICS. The amount of light that falls on a given area.

The three most common units for measuring ILLUMINATION are the footcandle, the lux and the phot.

ILS

Abbreviation for instrument landing system. See *instrument landing system.*



IMAGE

image \'im-ij\ *n.*

PHYSICS. A picture projected on a surface by a lens, or series of

lenses, or viewed directly by the eye through a lens; also, a reflection seen in, or projected by, a mirror.

The picture on a photographic film is a permanent impression of an IMAGE *projected by a lens.*

image orthicon \'im-ij 'ȯr-thi-ˌkän\

PHYSICS. A television camera tube in which a light image is focused on a transparent, photosensitive plate that emits electrons in proportion to the amount of light it receives.

The IMAGE ORTHICON *tube is 100 to 1,000 times more sensitive to light than its predecessor, the iconoscope.*

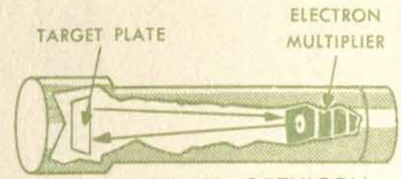


IMAGE ORTHICON (TUBE)

imaginary numbers \im-'aj-ə-ˌner-ē 'nəm-bərz\

MATHEMATICS. A complex number of the form a + bi, where a may be any real number, b may be any nonzero real number and i is defined to be the positive square root of -1, or $\sqrt{-1}$. If a = 0, the resulting imaginary number is a pure imaginary number.

Such numbers as $\sqrt{-3}$ *and* $\sqrt{-6}$ *are* IMAGINARY NUMBERS.

imaginary roots \im-'aj-ə-ˌner-ē 'rüts\

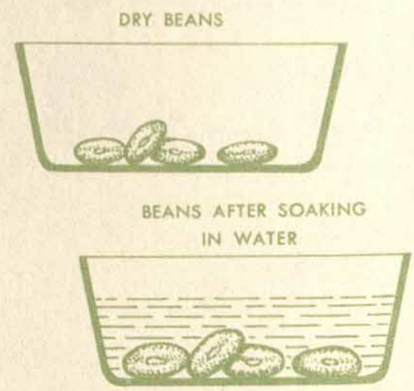
MATHEMATICS. The roots of an equation or of a number that are complex numbers in which the imaginary part is not zero.

The IMAGINARY ROOTS *of the equation* $x^2 + 49 = 0$ *are* $-7i$ *and* $+7i$.

imbibition \ˌim-bə-'bish-ən\ *n.*

BIOLOGY. Absorption of water by substances such as cellulose (as in plant cells) and gelatin, causing them to swell.

Shellac is used to prevent the IMBIBITION *of water by wooden objects.*

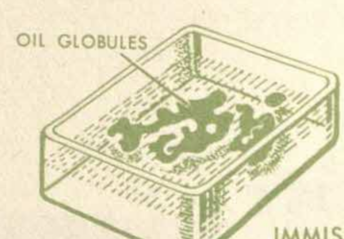


IMBIBITION

immiscible \(')im-'(m)is-ə-bəl\ *adj.*

CHEMISTRY. Referring to liquids that will not mix or blend with each other.

Kerosene and water are IMMISCIBLE.



IMMISCIBLE

immunity \im-'yü-nət-ē\ *n.*

MEDICINE and PHYSIOLOGY. The ability of an organism to resist or overcome a disease to which members of its species are usually susceptible; also, the ability to overcome certain toxins or poisons, such as those from a bee sting or mosquito bite.

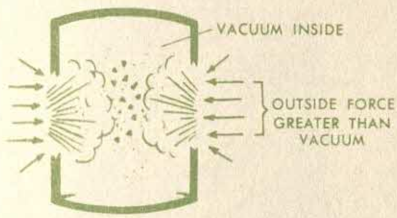
The thymus gland produces antibodies that give IMMUNITY *from several diseases of infancy.*

immunology \ˌim-yə-'näl-ə-jē\ *n.*
MEDICINE. The study of the way animals and plants resist, or become immune to, disease-producing organisms.

Many epidemic diseases have been nearly eradicated through advances in IMMUNOLOGY.

impact velocity \'im-ˌpakt və-'läs-ət-ē\
PHYSICS. In ballistics, a standard comparison for guns in which the speed of a bullet fired from a gun is measured at a given distance from the gun.

With all other conditions equal, the longer a gun's barrel, the greater the IMPACT VELOCITY *of a bullet fired from it.*



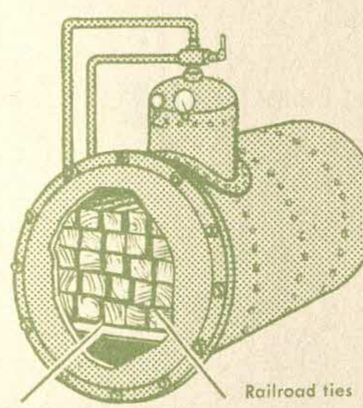
IMPLOSION

impedance \im-'pēd-ᵊnts\ *n.*
PHYSICS. An apparent force that opposes the action causing it; usually, the apparent force that resists the passage of alternating electric current through a circuit. This resistance is caused by the combined effect of electrical resistance and reactance.

Because a coil's IMPEDANCE *is greater than its resistance, less alternating current than direct current of the same voltage will flow through it.*

impermeable \(')im-'pər-mē-ə-bəl\ *adj.*
Referring to that quality of a substance that prevents specific materials from spreading into or through it.

Rubber is IMPERMEABLE *to water and air.*



IMPREGNATION (OF WOOD)

implication \ˌim-plə-'kā-shən\ *n.*
MATHEMATICS. A compound statement or proposition of the "if . . . then" form. The statement following the word "if" is known as the hypothesis, and the one following the word "then" is the conclusion.

An IMPLICATION *is false only when it has a true hypothesis and a false conclusion.*

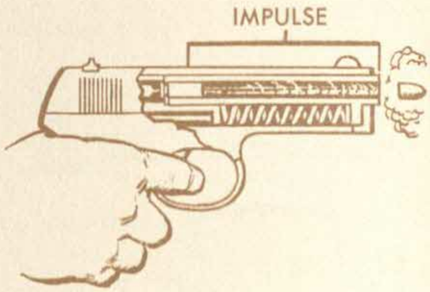
implosion \im-'plō-zhən\ *n.*
PHYSICS. A violent shattering as a result of force exerted from the outside of a hollow object toward the inside; a sudden collapsing inward.

An IMPLOSION *may occur when air pressure outside a vacuum bottle crushes its walls.*

impregnation \ˌim-ˌpreg-'nā-shən\ *n.*
1. CHEMISTRY. Saturation of a solid with a liquid. 2. ANATOMY

and ZOOLOGY. Fertilization of an ovum. 3. EARTH SCIENCE. A scattering of mineral ore through rock, rather than in a solid vein.

IMPREGNATION *of wood with creosote will slow the wood's decay.*



improper fraction \(')im-'präp-ər 'frak-shən\
MATHEMATICS. In arithmetic, a fraction whose numerator is equal to, or larger than, its denominator; also, in algebra, a fractional expression whose numerator has an equal or higher degree than its denominator.

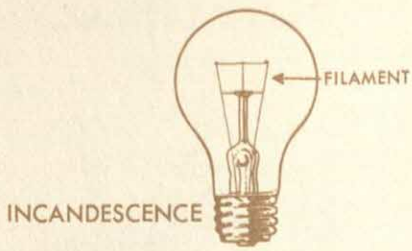
The expression $\frac{4}{3}$ *is an* IMPROPER FRACTION.

impulse \'im-ˌpəls\ *n.*
1. PHYSICS. A quantity that represents the change in momentum of an object, produced by a specific force for a given time. 2. PHYSIOLOGY. The electrical activity along nerve fibers, resulting from stimulation.

The IMPULSE *given to a bullet is limited by the short time the bullet is contained within the barrel after firing.*

inactive \(')in-'ak-tiv\ *adj.*
CHEMISTRY. Referring to a substance that does not react readily with most other substances at ordinary temperatures but that may react at high temperatures or in the presence of a catalyst.

Nitrogen is INACTIVE *at ordinary temperatures, but at the temperature of burning magnesium it becomes active and will react with magnesium.*

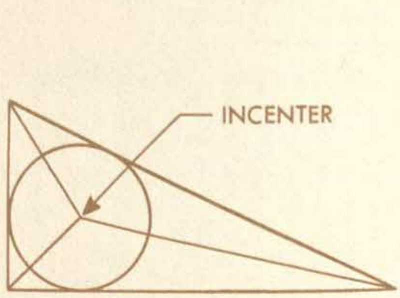


inbreeding \'in-'brēd-iŋ\ *n.*
BIOLOGY. Repeated crossing of organisms of the same family line, resulting in a strain of individuals with predictable characteristics.

INBREEDING *and crossbreeding are used to produce hybrid corn.*

incandescence \ˌin-kən-'des-ᵊnts\ *n.*
PHYSICS. The glow or radiation given off by an object that has been heated to a high temperature. Incandescence may occur in a solid, a liquid or a gas.

Light given off by an ordinary lamp bulb is caused by the INCANDESCENCE *of the metal filament within the bulb.*



incenter \'in-ˌsen-tər\ *n.*
MATHEMATICS. The center of a circle inscribed in a polygon.

The INCENTER *of a triangle is the point at which the bisectors of the angles of the triangle are concurrent.*

inch \'inch\ *n.*
MATHEMATICS. A unit of linear measure equal to 1/12 foot.

An INCH *is equal to 2.54 cm.*

incident beam of light \'in(t)-səd-ənt 'bēm əv 'līt\
PHYSICS. A beam of light that strikes the surface of an object or a substance.

The amount of refraction of light by glass depends on the angle of the INCIDENT BEAM OF LIGHT.

incisor \in-'sī-zər\ *n.*
ANATOMY and ZOOLOGY. Any one of the single-rooted front teeth that are located in the center of both the upper and lower jaws.

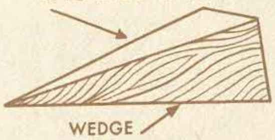
An INCISOR *is used to cut food into smaller parts as it is taken into the mouth.*

inclination \ˌin-klə-'nā-shən\ *n.*
1. ASTRONOMY. The angle created by the intersection of the plane of an orbit and the plane of the orbit of the earth. 2. Deviation from the vertical or horizontal.

The INCLINATION *of Mercury's orbit is 7 degrees.*

inclined plane \in-'klīnd 'plān\
ENGINEERING and PHYSICS. A flat surface, slanting upward, along which an object may be slid in order to decrease the force needed to lift the object; one of the simple machines.

An INCLINED PLANE *has many practical uses.*



included angle \in-'klüd-əd 'aŋ-gəl\
MATHEMATICS. The angle formed by two designated sides of a polygon.

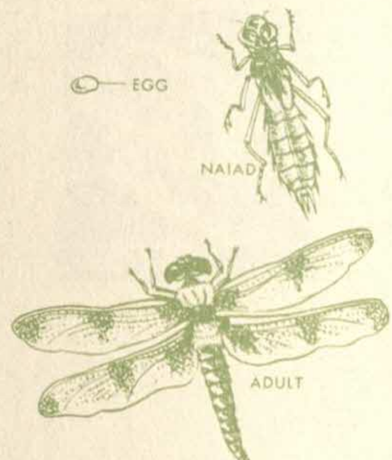
Two triangles that have two sides and the INCLUDED ANGLE *equal are congruent.*

incomplete dominance \ˌin-kəm-'plēt 'däm-(ə-)nən(t)s\
BIOLOGY. A characteristic of some pairs of genes when neither is totally dominant nor totally recessive, and the traits of each are blended and passed on to offspring. For example, crossed red and white flowers may produce pink flowers instead of red or white ones.

INCOMPLETE DOMINANCE *is one exception to Mendel's laws of heredity.*

incomplete metamorphosis \\ˌin-kəm-'plēt ˌmet-ə-'mȯr-fə-səs\\
ZOOLOGY. The kind of development among several groups of insects in which the immature forms, called naiads, are adapted to an aquatic life and then change into the terrestrial adult stage without passing through a resting stage.

In the INCOMPLETE METAMORPHOSIS *of mayflies, the naiads live for years, while the adults live for about one day.*



INCOMPLETE METAMORPHOSIS

increment \\'iŋ-krə-mənt\\ *n.*
1. MATHEMATICS. The difference in the numerical value of a variable as it changes from a given value to a greater or smaller value. 2. An increase.

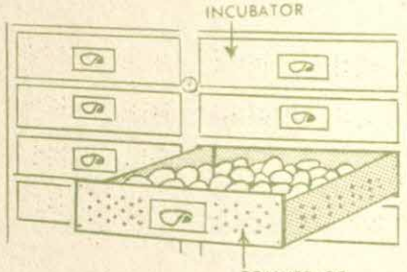
In calculus, an INCREMENT *in the variable x is generally designated by the symbol* $\triangle x$.

incubation \\ˌiŋ-kyə-'bā-shən\\ *n.*
1. BIOLOGY. Inducing the development of fertilized eggs by the application of heat. 2. MEDICINE. The period between the time an infection enters the body and the first appearance of the symptoms of the disease.

Artificial INCUBATION *of chicken eggs is often used in modern hatcheries.*

independent assortment \\ˌin-də-'pen-dənt ə-'sȯ(ə)rt-mənt\\
BIOLOGY. A term referring to inherited characteristics, each trait being a separate entity not influenced by the expression or suppression of any other trait. For example, the tendency for blue eyes may be inherited along with either straight hair or curly hair.

Gregor Mendel discovered the law of INDEPENDENT ASSORTMENT *when he realized that characteristics can separate and combine again in different ways in different generations.*



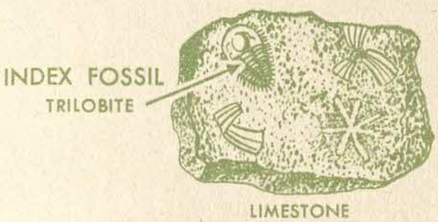
INCUBATION

independent variable \\ˌin-də-'pen-dənt 'ver-ē-ə-bəl\\
MATHEMATICS. The symbol used to denote any member of the domain of a function; thus, the symbol appearing as the first entry of the ordered pair that defines a function; also, a symbol to which different values chosen from the domain of the function may be assigned and from which the corresponding values of the dependent variable are computed.

In the function $f = (x, y)$, *where x is a real number and* $y = 8 - x$, *x is the* INDEPENDENT VARIABLE.

index \\'in-ˌdeks\\ *n.*
MATHEMATICS. A symbol showing the power or root of a number.

In the expression 4^2, ^{2} *is an* INDEX *indicating that 4 is squared.*



index fossil \ˈin-ˌdeks ˈfäs-əl\

EARTH SCIENCE. Any fossil found only in rocks of a specific geologic age; a guide fossil.

An INDEX FOSSIL *is most useful in establishing the age of a rock stratum.*

index number \ˈin-ˌdeks ˈnəm-bər\

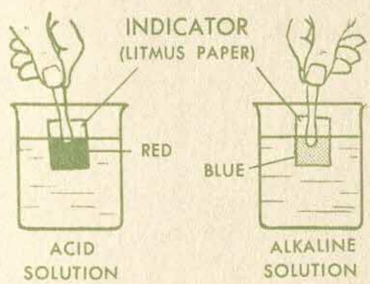
MATHEMATICS. In statistics, the value of a quantity, usually its cost, used as a base level with which related values over a period of years can be compared.

The INDEX NUMBER *is usually based on 100.*

index of refraction \ˈin-ˌdeks əv ri-ˈfrak-shən\

PHYSICS. A number expressing the relative amount of change of direction a beam of radiation undergoes when passing from a vacuum into a given transparent substance, or from one substance into another.

The unusual sparkle of diamonds is caused in part by their high INDEX OF REFRACTION.



indicator \ˈin-də-ˌkāt-ər\ *n.*

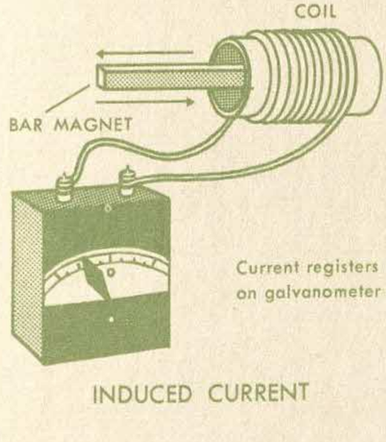
CHEMISTRY. Any substance present in a chemical reaction or solution that shows, usually by a color change, something about the reaction or the conditions in the solution. An indicator is frequently used to determine the acid or alkaline nature of a solution.

The juice from grapes or red cabbage may act as an INDICATOR *when placed in acid or alkaline solutions.*

induced current \in-ˈd(y)üst ˈkər-ənt\

PHYSICS. An electrical current set in motion through a conductor by a magnetic field moving or varying relative to the conductor.

One can produce an INDUCED CURRENT *in a circuit that contains a coil by moving a bar magnet.*



INDUCED CURRENT

induction \in-ˈdək-shən\ *n.*

1. PHYSICS. The production of an electric charge or magnetic field in an object caused by the object's being near an electrically-charged body or in a magnetic field originating in another object. 2. The process of reasoning from the particular to the general.

An iron rod laid in a north-south direction on the earth's surface may become noticeably magnetized by INDUCTION *after several weeks.*